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Contents

Equilibrium between Soil and Electrolytes, and Its Influence upon Some Lime Requirement Methods. NORMAN ASHWELL CLARK AND EMERSON R. COLLINS 417

The Nature of Calcium Hydroxide Absorption by Hydrated Silica. W. M. SHAW AND W. H. MACINTIRE 429

The Results of X-Ray and Microscopical Examinations of Soil Colloids. STERLING B. HENDRICKS AND WILLIAM H. FRY 457

Properties of Organic Hardpan Soils with Special Reference to Their Formation. L. A. RICHARDSON 481

Index 489

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EQUILIBRIUM BETWEEN SOIL AND ELECTROLYTES, AND ITS INFLUENCE UPON SOME LIME REQUIREMENT METHODS

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The fact that existing methods for the determination of lime requirements of soil (e.g. Veitch, Hutchinson and MacLennan) are not only tedious but also give results which are frequently unsatisfactory, has caused from time to time a further study of the question. Some attempt was made to correlate pH values with the amount of lime needed, but as more knowledge accumulated concerning the soil constitution, it was seen that correlation here could be fortuitous only. Titration of the soil to pH 7 with a base held out more possibilities, and recently a number of different procedures has been suggested. An investigation of some of these methods has been made, and a comparison on Iowa soils is reported in this paper.

A simple titration method—mixing the soil with sufficient $Ca(OH)_2$ to bring it to pH 7—was used by Sharp and Hoagland (20), who noted that there was a slow equilibrium, due to the probable insolubility of the acid-forming constituents of the soil, and that shaking was needed. The results agreed well when soils were mixed with the indicated lime and incubated. Fisher (10) in 1921 pointed out that this was not altogether satisfactory and that it did not investigate completely the soil reaction, partly because it measured only titratable acidity and partly because of "adsorptive" and other buffer effects. He found that Hutchinson and MacLennan's method gave from 3 to 22 times as much lime requirement as the colorimetric determination of pH [$Ba(OH)_2$ to pH 7] on the centrifugate. Crowther and Martin (9) state that even Hutchinson and MacLennan's method underestimates the lime needed to give a neutral soil in practice, and that this method also calls for less lime than is found necessary by electrometric titration with $Ca(OH)_2$ to give a neutral suspension of the soil. Brioux (3) in 1928 compared the Hutchinson-MacLennan method with the pH values of the soil after adding increasing amounts of lime water, and found the results agreed within 0.02 per cent, except with soils of high humus content.

Christensen and Jensen (5) correlated the laboratory method and the reaction of soils in the field. They compared the results from titration by $Ca(OH)_2$ with field trials obtained by mixing the indicated amount of lime in the soil. They concluded that on their Danish soils at least three times the amount of lime indicated by the titration was needed to give the reaction desired in the field. Hissink and van der Spek (13), working with humus soils, compared $Ba(OH)_2$ with $Ca(OH)_2$ and NaOH as the titrating agents. Sodium was distinctly lower in the figures found for the lime requirement, and by checking the pH of plots of the same soil, both limed and unlimed, these investigators decided that the results with $Ca(OH)_2$ were nearest the truth. They point out that the speed of the reaction depends both upon the

[1] Contribution from the department of chemistry.

nature of the soil and the fineness of the carbonate, and also that the figures obtained are minimal amounts, as part of the $CaCO_3$ is used by plants, part remains as $CaCO_3$, and some is removed by rain.

The simple titration of soil with bases has been further criticized adversely because it indicates the dissolved hydrogen but removes little of the exchangeable hydrogen from the complex (11). Crowther and Martin (9) added 0.1 *N* $CaCl_2$ to a soil suspension along with $Ca(OH)_2$, and found a higher lime requirement than with the hydroxide alone—the higher concentration of the Ca ion enabling more H to be removed from the complex. Daikuhara's method, however, as used by Christensen and Jensen (5) (treating the soil with *N* KCl and titrating the extract with NaOH) gave a smaller lime requirement than a titration curve with $Ca(OH)_2$ on the soil suspension.

Trénel (22) used a 0.1 *N* KCl suspension and found that the pH was proportional to the titration values of *N* KCl extracts. Hardy and Lewis (11) in 1929 suggest that the soil suspension in a neutral $CaCl_2$ solution (they used 0.4 *N* $CaCl_2$, as higher concentrations introduced a salt error in the pH determined by the quinhydrone method) should be titrated with $Ca(OH)_2$ to pH 7, in order to obtain both the hydrogen on the complex and in the solution. This method gave a lime requirement usually larger than Hutchinson and MacLennan's, but the results were more uniform on the soils investigated. They further point out that 100 per cent saturation with bases, that is the removal of all the hydrogen from the complex, does not necessarily correspond to neutrality. [Compare Hissink's soils often less than 50 per cent saturated at pH 7 (12) and Bradfield's 100 per cent neutralization of clays only at pH 10–11 (2).]

In contrast to the need for titration of the soil suspension in salt solutions as shown by Crowther and by Hardy and Lewis, Ramann (17) states that the reaction between soil and KOH gives a rapid and complete replacement of the absorbed hydrogen, and Parker (16) titrating with $Ba(OH)_2$ to pH 7, allowing 2 to 3 days for equilibrium, finds that the amount of hydrogen which is neutralized checks the hydrogen on the complex determined by two other methods. This indicates, therefore, that there is complete removal of the hydrogen on the complex by the titration. Similarly, Saint (18) shows that a soil may behave like a simple weak acid and that the reaction between the hydroxide and the exchange hydrogen ions is rapid and complete, although this is accompanied by hydrolysis. Kelly and Brown (14) deny the hydrolysis of the calcium complex. Saint concludes that the neutralization is followed by a further adsorption of the base by the soil. De'Sigmond and di Gleria (21) obtained these same two stages, both on soils and on artificial zeolites, by titration with $Ba(OH)_2$—at first an instant reaction to the neutral point of the complex, followed by a slow adsorption for three days. There is, therefore, a distinct difference of opinion as to the action of the hydroxide with and without the presence of a neutral salt.

A further point on which there is little unanimity is the time required to bring the soil to equilibrium with the hydroxide. Sharp and Hoagland (20) pointed out that on titrating with $Ca(OH)_2$, shaking is needed and that equilibrium is slow. Crowther (8) shows that equilibrium with alkaline solutions is most rapid when the shaking is done with finely divided samples, but that with other soils approximately constant values are obtained after a few hours if the final solution is still acid. Hissink and van der Spek (13) in their studies on humus soils found a slow equilibrium, which they ascribe to the gradual peptization of the humus, as Bradfield (2) had reported almost instantaneous equilibrium with colloidal clay of acid soils. They choose 72 hours for their reaction time in the soil titration. Burgess (4) gives the optimum time of shaking for the water suspension as 30 minutes, and Maiwald (15) agrees with Hissink and van der Spek that for titration 72 hours is needed with intermittent shaking, and that beyond this there is little change in the reaction. On the other hand, Hardy and Lewis (11), with a suspension of soil in calcium chloride, shaken and allowed to stand overnight before being titrated with the $Ca(OH)_2$, report that in most cases there is no difference from one minute to several days, and that the shaking which is needed for the actual titration is less than 3 minutes, unless large amounts of hydroxide are added at a time.

A comparison of the three ways follows: titration of the soil-water suspension with $Ca(OH)_2$—Christensen and Jensen, Hissink, Brioux; titration of the soil suspension in $CaCl_2$ solution with $Ca(OH)_2$—Crowther, Hardy, and Lewis; and titration of the suspension in NaCl by NaOH—a different cation to compare with Trénel and Daikuhara's KCl.

TABLE 1

*Description of soils**

NUMBER	SERIES	CLASS	ORIGIN AND LOCATION	COLOR	DRAINAGE	pH ON MIXING 1:5	pH AFTER 90 HOURS STIRRING
1	Bremer	Silt loam	Terrace	Dark brown	Poor	7.0	7.5
2	Buckner	Fine sandy loam	Terrace	Brown	Good	5.6	5.7
3	Carrington	Loam	Drift	Brown	Satisfactory	5.6	6.6
4	Clarion	Loam	Drift	Light brown		7.5	7.8
6	Clyde	Silty clay loam	Drift	Black	Poor	7.6	7.6
7	Conover	Silt loam	Drift	Grayish brown	Fair	5.6	5.6
8	Fargo	Silty clay loam	Terrace	Brownish black	Poor	7.2	7.6
9	Fayette	Silt loam	Loess	Grayish brown	Slow	5.7	6.0
10	Lamoure	Silty clay loam	Swamp and bottomland	Dark brown	Poor	7.8	7.7
11	Lindley	Fine sandy loam	Drift	Grayish brown	Excellent	5.9	6.8
12	Millsdale	Loam	Terrace	Brown	Good	6.2	6.8
13	Muscatine	Silt loam	Loess	Black	Poor	7.8	8.0
14	O'Neil	Sandy	Terrace	Brown	Good	6.9	7.9
15	Peat			Black	Poor	7.3	7.4
16	Sarpy	Fine sandy loam	Swamp and bottomland	Brown	Good	7.8	7.9
17	Shelby	Loam	Drift	Brown	Good	5.9	6.5
18	Sioux	Sandy	Terrace	Brown	Good	8.2	8.1
19	Tama	Silt loam	Loess	Dark brown	Good	5.5	5.7
20	Wabash	Silt loam	Bottomland	Dark brown		7.8	7.9
21	Waukusha	Loam	Terrace	Brownish black	Adequate	5.5	5.7
22	Webster	Silty clay loam	Drift	Dark brown		7.9	8.0

* Data taken from soil survey maps of the respective counties.

EXPERIMENTAL

The 21 soil types are described in table 1 (no. 5 was lost and therefore is not included). The data, except the pH values, are from the soil survey reports of Iowa and from observation. The pH values, taken on mixing with water ratio 1:5 and after 90 hours stirring, are included.

The quinhydrone electrode was used for the determination of pH as described by Clark and Collins (6) except that the Schollenberger electrode (19) was sub-

stituted to eliminate the agar bridge. This electrode needs a very closely fitting ground glass joint, but with careful grinding a joint can be obtained which shows no diffusion when immersed in distilled water and held to the light, and which yields no trace of cloudiness in a silver nitrate solution after several minutes stirring. Figure 1 shows the electrode. The platinum and the stirrer are placed somewhat below the glass joint. The soil suspension can then be mixed with the quinhydrone by the stirrer before contact is made with the KCl; the container is then pushed up and the reading taken on the stirred suspension. This gives a very constant reading in almost all cases.

Many of the results reported on titration values have been obtained by shaking by hand or intermittently. Since different fractions settle out at different rates, all fractions may not be in contact with the solution of the same concentration. Comber (7) has pointed out that there may be a difference between the concentration of the hydrogen ion in the liquid inside and outside the soil crumb. Baver (1) and Clark and Collins (6) have shown the efficiency of a stirrer in breaking up the soil crumb. A stirring apparatus was therefore devised as shown in plate 1. In the apparatus the mouth of the flask was pressed against a rubber pad and this effectively prevented the entrance of air except at the time of sampling. The soil was placed in the flasks with the solution to be used, ratio 1 of soil to 5 of solution; samples were removed as required, while stirring, by means of a 25 cc. pipette, and the pH was determined by the quinhydrone electrode shown in figure 1.

The results indicate that there is no definite time for equilibrium which holds with all soils, either with $Ca(OH)_2$ alone or with neutral salts. For example, soil no. 1, which had a pH of 7.0 in water suspension, taken directly after mixing, produced a pH of 8.4 when 0.005*N* $Ca(OH)_2$ was added (ration 1 soil to 5 solution), and took 40 hours to drop to 7.5, after which it stayed constant to 120 hours. Soil no. 16 with an alkaline reaction (pH 7.8 in water suspension) had a pH of more than 8.5 when mixed with the $Ca(OH)_2$, but dropped steadily through the whole 120 hours. Soil no. 2 (pH 5.6) gave a pH of 8.0 with $Ca(OH)_2$ and dropped rapidly for 10 hours to pH 7.1, reaching 7.0 in 85 hours. The time curves (pH on hours) show varied shapes. In general, the change after 90 hours is very small.

When the neutral salt solution is added, the alteration of pH is much quicker in most cases, especially with the smaller concentration of the hydroxide. Figure 2 shows the set of curves for an acid soil (no. 12). Figure 3 gives the curves for a soil approximately neutral (no. 1) and figure 4 for an alkaline soil (no. 10). It will be seen that even with the neutral salts there is a change over a considerable range of time.

From the figures obtained in this way the curves for the buffer action of the soils can be plotted. These are found to be smooth curves both in water suspension and in the neutral salt solutions. Maiwald (15), who investigated carefully the buffer action of carbonate-poor soils, obtained smooth curves of the same kind, as did also Crowther (8) and Brioux (3). Figure 5 shows a typ-

ical set of buffer curves for an acid soil (no. 9)—the pH is plotted at 0, 10, and 90 hours on the normality of the $Ca(OH)_2$ or NaOH in the suspension.

Table 2 gives the normality of the hydroxide required to bring the suspension to pH 7, taken from the buffer curves. The titration in calcium chloride suspension has the largest lime requirement in all cases at 90 hours, whereas the sodium chloride demand is considerably greater than the water suspension. In almost every case the requirement after 90 hours' stirring is larger than at 0

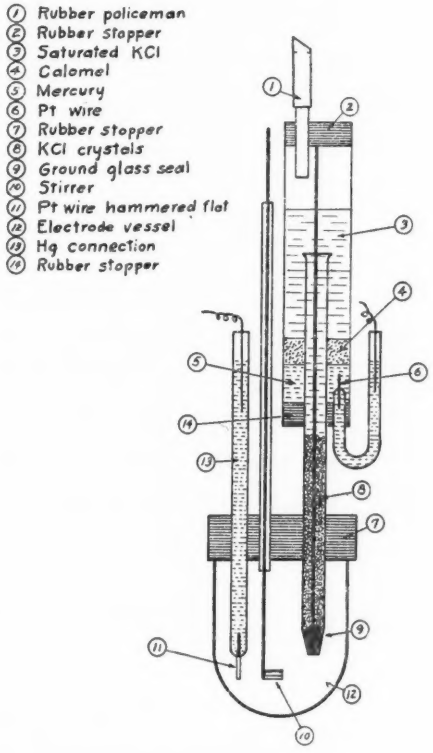

FIG. 1. QUINHYDRONE ELECTRODE

or 10 hours. In 15 of the 21 soils there is a lime requirement by the $CaCl_2$ suspension at 90 hours, whereas, with the titration in water suspension, taken directly after mixing, there is a demand in only 9 of the soils.

In view of the fact that Christensen and Jensen (5) find that approximately three times as much lime is needed in practice as is found by titrating with $Ca(OH)_2$ alone, the ratio of the requirement in $CaCl_2$ suspension to that shown in water suspension is given in table 3.

The figures for the ratio of the lime requirements in the $CaCl_2$ at the time of mixing, to those in the water suspension, also on mixing, are thus in general close to Christensen and Jensen's value of 3 to 1. The ratio after 90 hours

TABLE 2

Normality of hydroxide required to bring suspension to pH 7 (soil: solution = 1: 5)

SOIL NUMBER	NORMALITY REQUIRED								
	Water suspension			0.4*N* $CaCl_2$ suspension			0.4*N* NaCl suspension		
	0 hour	10 hours	90 hours	0 hour	10 hours	90 hours	0 hour	10 hours	90 hours
1	.....	.....	.....	0.004	0.009	0.011	0.007	0.006	0.002
2	0.003	0.005	0.005	0.010	0.011	0.012	0.009	0.010	0.011
3	0.003	0.005	0.003	0.010	0.012	0.012	0.011	0.011	0.011
4	.....	.....	.....	0.000	0.001	0.001	.....	.....	.....
6	.....	.....	.....	0.003	0.005	0.002	.....	.....	.....
7	0.006	0.008	0.009	0.012	0.014	0.015	0.012	0.013	0.013
8	.....	.....	.....	0.002	0.004	0.004	0.003	0.002	0.000
9	0.004	0.005	0.005	0.010	0.012	0.014	0.010	0.010	0.012
10	.....	.....	.....	.....	.....	.....	.....	.....	.....
11	0.001	0.002	0.001	0.008	0.008	0.010	0.009	0.009	0.009
12	0.002	0.001	0.001	0.005	0.008	0.009	0.008	0.008	0.008
13	.....	.....	.....	.....	.....	.....	.....	.....	.....
14	.....	.....	.....	0.001	0.003	0.003	0.002	0.001	0.000
15	.....	.....	.....	0.006	0.007	0.005	0.002	0.002	0.000
16	.....	.....	.....	.....	.....	.....	.....	.....	.....
17	0.002	0.004	0.003	0.006	0.010	0.011	0.010	0.010	0.010
18	.....	.....	.....	.....	.....	.....	.....	.....	.....
19	0.006	0.010	0.012	0.014	0.019	0.021	0.015	0.016	0.017
20	.....	.....	.....	.....	.....	.....	.....	.....	.....
21	0.006	0.009	0.008	0.013	0.017	0.019	0.013	0.015	0.015
22	.....	.....	.....	.....	.....	.....	.....	.....	.....

TABLE 3

Ratio of lime requirement in salt solutions to that in water suspensions

	SOIL NUMBER								
	1	3	7	9	11	12	17	19	21
At 90 hours in $CaCl_2$ suspension to water suspension at mixing.....	4.0	4.0	2.5	3.5	10.0	4.5	5.5	3.5	3.2
At mixing, both in $CaCl_2$ and water suspensions.....	3.1	3.1	2.0	2.5	8.0	2.5	3.0	2.3	2.2
At mixing, both in NaCl and water suspensions.....	3.0	3.3	2.0	2.5	9.0	4.0	5.0	2.5	2.2

stirring in the $CaCl_2$ is somewhat higher. Soil no. 11 is an exception, with a much higher ratio, due to the low buffer capacity of the soil—a small addition of $Ca(OH)_2$ to the water suspension gives a very large increase in pH. Titration in sodium chloride suspension shows a somewhat lower ratio in almost all

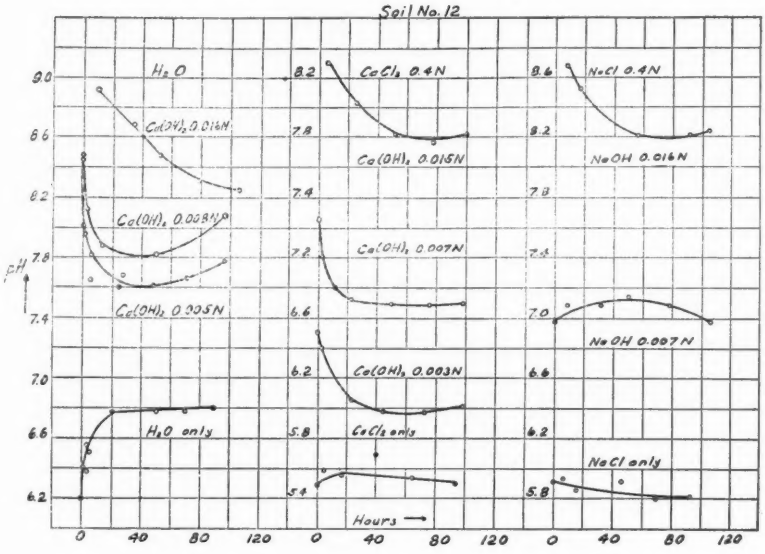

FIG. 2. pH VALUES OF AN ACID SOIL (No. 12), IN WATER, IN 0.4 *N* $CaCl_2$, AND IN 0.4 *N* NaCl SUSPENSIONS WITH VARYING QUANTITIES OF HYDROXIDE

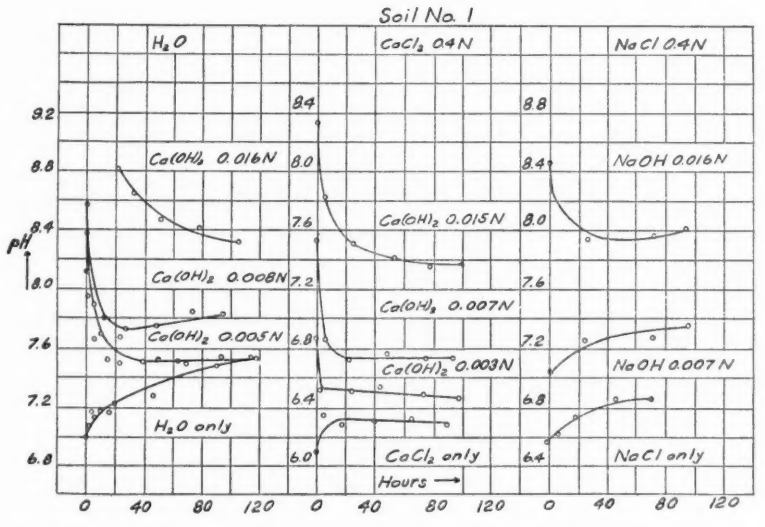

FIG. 3. pH VALUES OF A SOIL APPROXIMATELY NEUTRAL (No. 1), IN WATER, IN 0.4 *N* $CaCl_2$, AND IN 0.4 *N* NaCl SUSPENSIONS WITH VARYING QUANTITIES OF HYDROXIDE

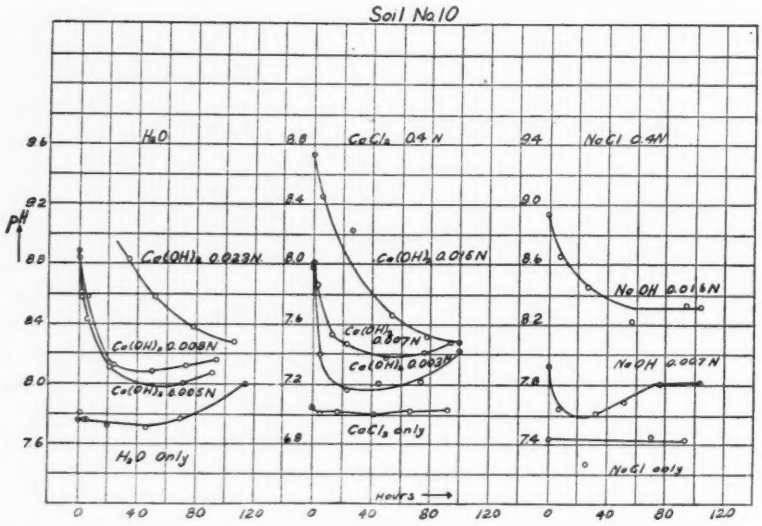

FIG. 4. pH VALUES OF AN ALKALINE SOIL (No. 10), IN WATER, IN 0.4 *N* $CaCl_2$, AND IN 0.4 *N* NaCl SUSPENSIONS WITH VARYING QUANTITIES OF HYDROXIDE

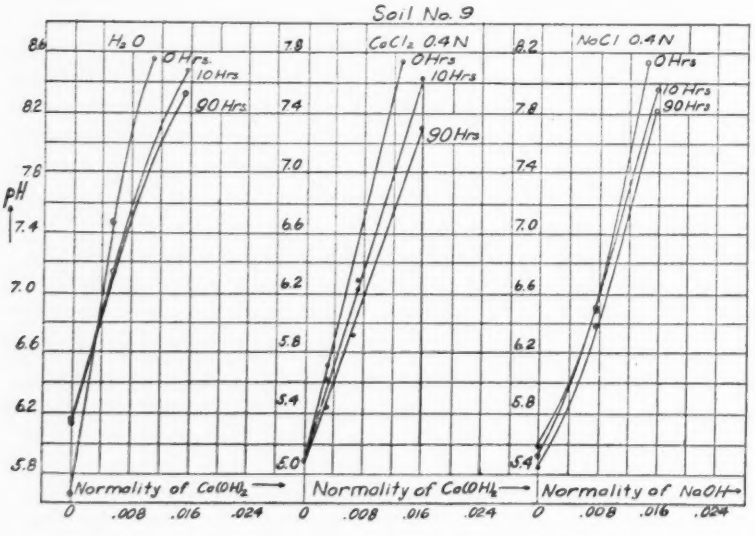

FIG. 5. BUFFER CURVES FOR AN ACID SOIL (No. 9), IN WATER, IN 0.4 *N* $CaCl_2$, AND IN 0.4 *N* NaCl

cases, and there seems to be no advantage, therefore in changing from calcium to sodium.

With regard to the assertion of Saint and of de' Sigmond and di Gleria that on addition of the hydroxide to the water suspension there is first an instant neutralization and then a slow adsorption, this neutralization does not seem to extend to the hydrogen on the soil complex. In all cases there was a rapid rise in the pH when the $Ca(OH)_2$ was added, followed by a drop which varied in speed and extent with the different soils. This would be expected if there was a neutralization followed by the slow adsorption as suggested, but even when there was not sufficient hydroxide added to bring the suspension to pH 7 the drop in pH followed as before. In addition, the presence of the $CaCl_2$ invariably produced a lower pH for the same amount of hydroxide, indicating a further removal of hydrogen ions from the complex. That the whole of the hydrogen is removed at once by the simple titration with hydroxide seems therefore to be very doubtful; de 'Sigmond and di Gleria, however, are inclined to question the existence of hydrogen on the complex above pH 7 (21).

SUMMARY

Titration methods for the determination of lime requirements of soils have been investigated. A comparison has been made on 21 Iowa soils of varied pH, by titration with $Ca(OH)_2$ on the soil suspension in water and in $CaCl_2$ solution, and with NaOH in NaCl solution. The soils were stirred continuously instead of being shaken; samples were removed and the pH measured by the quinhydrone method.

The time of equilibrium varied with the soil, but there was little change after 90 hours. Generally, equilibrium was more rapid in the salt suspensions.

Lime requirements of the soils in $CaCl_2$ and NaCl suspensions were much higher than in water suspensions. With one exception, the requirement by the $CaCl_2$ suspension, measured on mixing, was from 2 to 3 times as great as that by titration with $Ca(OH)_2$ alone; measured at 90 hours, the requirement was 2.5 to 5.5 times as great. These figures are in the order of Christensen and Jensen's measurements, in which they found approximately 3 times as much lime was needed in the field as was shown by the simple titration method with $Ca(OH)_2$.

The results do not indicate that the instantaneous neutralization suggested by Saint and by de 'Sigmond and di Gleria extends to the total hydrogen on the complex.

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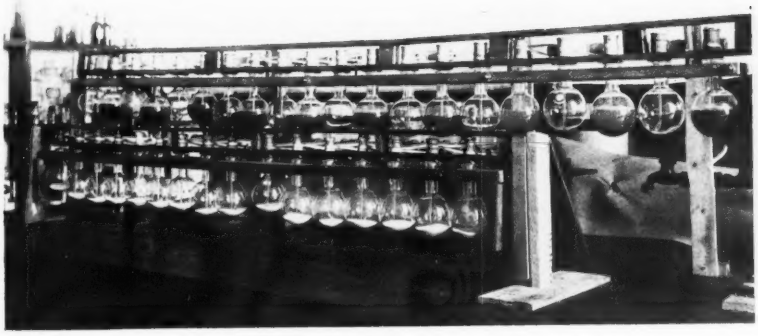

STIRRING APPARATUS

THE NATURE OF CALCIUM HYDROXIDE ABSORPTION BY HYDRATED SILICA

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Hydrated silica may be considered as of universal occurrence in rock-derived soils, even though its rôle in the soil system is not well known. The weathering and hydrolytic disintegration of rocks result in the liberation of some hydrated silica, and a continuous production of its reactive forms may be expected because of the dynamic conditions that prevail in a soil system. On the other hand, there may be considerable outgo of colloidal silica through leaching during the seasons when the electrolyte content of the percolates is low. Plants can also take up large quantities of hydrated silica, as has been demonstrated by Jennings (7) and others.

It has been pointed out (12, 19) that the reactive capacity of silicic acid has probably been under-evaluated and that mechanical manipulation and removal of organic matter through treatment with hydrogen peroxide may influence the reactivity of the silica in a soil system (17). The proportion of added lime to soil mass and the rapid carbonation of $Ca(OH)_2$ (13) delimit the magnitude of the lime-silica reactions in practice to an extent that does not obtain for many experimental conditions. The nature of lime-silica reactions is involved when lime water is used to determine base-saturation capacity and similar values.

In an attempt to explain certain fixations that had been encountered in heavily limed soils (20, 21, 22) suspensions of pure oxides of silicon, aluminum, and iron, had been used with aqueous solutions of $Ca(OH)_2$-$CaSO_4$ (16). The reactivity of the silica and alumino silicates in aqueous $Ca(OH)_2$-$CaSO_4$ solutions (17) has been shown to produce certain acid-soluble end products that might well serve as a measure of the colloidal silica and colloidal alumina in a soil system. The present contribution is the result of further studies of the lime-silica reactions in an attempt to utilize them in carrying out soil absorption researches.

PREVIOUS OBSERVATIONS

No report of a systematic study of the absorptive capacity of hydrated silica for $Ca(OH)_2$ has been found. Some attention, however, has been paid to the

[1] The analyses and computations were made by the senior author. The junior author is responsible for the presentation.

functions of silica and different silicate additions in the soil (5, 27, 14, 1, 23, 24, 29), and different aspects of the subject have been noted and data offered by Frear (4), Ramann (26), Van Bemmelen (30, 31), Jordis and Kanter (8), Klasse (9), Landrin (10), Lerch and Bogue (11), Comber (3), and Mattson (25).

Approaching the question from the standpoint of soil colloids, Vincent (32) reported that lime water caused the complete precipitation of silicic acid. The amorphous precipitate obtained by Vincent had a composition corresponding to the formula $SiO_2 \cdot 3CaO$. After the completion of the present experimental work, Baylis (2) presented a paper on the absorption of $Ca(OH)_2$ by silica gels of different degrees of hydration. His experimental procedure differed from that used by the present authors. Baylis summarized his conclusions in the statement:

> There appears to be a compound of calcium oxide and silica approximately equal to the hydrated $CaO \cdot SiO_2$ formed when calcium oxide is added to a solution containing silica in solid form such as hydrous oxide of silica. Calcium hydroxide, to the extent of approximately 30 to 45 per cent united with the silica, appears to be absorbed by the monocalcium silicate or whatever be the definite compound of CaO and SiO_2.

PRELIMINARY ABSORPTION EXPERIMENTS

Mode of agitation and attrition agents

Experiments were carried out to determine the procedure that would give the greatest speed of absorption during a 30-day period, as determined at successive 5-day intervals. Vigorous and continuous agitation of the lime-silica suspensions in a specially devised machine (27) was compared with intermittent agitation. Air-dried gel of 100-mesh fineness was prepared by the process of Holmes and Anderson (6). One-gram charges, containing 24.1 milliequivalents of SiO_2 were placed in 1,000-cc. Pyrex flasks, together with 1 gm. of CaO. A constant volume of 900 cc. of distilled water was added to each flask and the suspensions were agitated with and without the attrition agents. The suspensions were allowed to *settle overnight* and aliquots of 50 cc. were then titrated with 0.1 *N* HCl against phenolphthalein. The absorption of $Ca(OH)_2$ was calculated from progressive decreases in the titration values and volumes.

Continuous agitation without an attrition agent was found to be ineffective, the absorption during the first 5 days being about 45 per cent of the maximum, and sluggish thereafter. Quartz pebbles hastened absorption, but they abraded the flask surface severely, thus injecting finely-devided glass into the lime-water suspension and presenting also an increased and more active glass surface. When steel balls were used with only intermittent agitation the absorption was also incomplete. The greatest speed of actual absorption by the gel charge was obtained by continuous agitation, with $\frac{1}{8}$-inch steel balls as an attrition agent.

Influence of size of particle

The influence of the size of particles of the silica gel upon the efficiencies of the different modes of agitation and attrition agents was also considered. A more hydrated silica gel was prepared and dried, under more humid atmospheric conditions. The ground gel was screened between sieves of 12, 35, 100, and 200 mesh to obtain respective separates of 1.07, 0.30, 0.11, and 0.035 mm. The purity and the degree of hydration of each screening are given in table 1. A constant charge of 1.5 gm. of each gel separate was used. The CaO charges and volumes of water were the same as those previously stipulated. The three 15-day agitation procedures described in table 2 were compared, the sampling, titrations, and absorption calculations being the same as in the previous experiment.

The results of table 2 show the sea sand failed to effect any actual enhancement in the speed of the absorption, since, after correction for the sand blank,

TABLE 1

Partial analyses of the silica gel separates of table 2

SCREENED BETWEEN MESHES	AVERAGE DIAMETER OF SEPARATES	LOSS ON IGNITION PER CENT OF HYDRATED PRODUCT			RESIDUE FROM H F + H_2SO_4 VOLATILIZATION			SiO_2 CONTENT OF HYDRATED PRODUCT		DEGREE OF HYDRATION EXPRESSED AS H_2O: SiO_2 RATIO
		1	2	Ave.	1	2	Ave.	Per cent	M.e. per gram	
	mm.									
12–35	1.07	57.7	57.8	57.75	0.06	0.06	0.06	42.2	14.53	2.2
35–100	0.30	58.2	58.2	58.2	0.06	0.06	0.06	41.8	13.92	2.3
100–200	0.11	56.0	56.3	56.15	0.06	0.06	0.06	43.9	14.62	2.1
Through 200	0.035	54.2	54.0	54.1	0.15	0.13	0.14	45.8	15.25	2.0

the results were almost identical with those obtained in the corresponding experiments without attrition. The 12-mesh silica without attrition showed, after 15 days, an absorption of only 76 per cent of that found for the same separate with attrition by steel balls. Even with attrition, the coarsest mesh did not show the maximum absorption during the 15-day period. The 0.035-mm. gel attained practically its full absorptive capacity in 2 days with attrition, whereas without attrition the absorption was only about 80 per cent of maximum. Without attrition, the 100-mesh gel attained 91 per cent of the maximum absorption in the first 2 days and complete absorption in about 15 days. The 200-mesh gel with steel balls showed an absorption of 97 per cent of the maximum after 2 days and complete absorption in 5 to 10 days.

It therefore appears necessary to use a finely divided gel, 100- 200-mesh, with an attrition agent, if maximum absorption of $Ca(OH)_2$ by air-dried silica gel is to be attained within a period of 2 to 5 days. This procedure was adopted as the standard for subsequent studies.

The influence of varying degrees of gel-hydration

The influence of the degree of hydration upon the speed and extent of absorption of $Ca(OH)_2$ by silica gel during a 10-day period was next studied. For this purpose two laboratory-prepared gels, A and B, were used: the gel A had a H_2O: SiO_2 ratio of 1.33:1, whereas gel B had a ratio of 2.2:1. A hydrated silicic acid of the same water content as that of silica A and "glaucosil" were included. Two types of anhydrous silica were also used—

TABLE 2

*Efficiencies of different modes of agitation in promoting reaction between $Ca(OH)_2$ and the different separates of a silica gel**

MODE OF AGITATION	AVERAGE DIAMETER OF SEPARATES	0.1 *N* HCl TITRATION PER 50 CC. AFTER CONTACT OF				ABSORPTION OF $Ca(OH)_2$ EXPRESSED AS M.E. AFTER CONTACT OF			
		2 days	5 days	10 days	15 days	2 days	5 days	10 days	15 days
	mm.	*cc.*	*cc.*	*cc.*	*cc.*				
A†	1.07	12.60	11.50	10.60	9.40	11.88	13.75	15.19	16.99
B‡	1.07	8.00	7.40	7.00	6.60	20.16	21.18	21.82	22.42
C§	1.07	12.30	.....	(lost)	.....	12.42	.....	(lost)	.....
A	0.30	9.40	8.50	7.70	7.10	17.64	19.17	20.45	21.35
B	0.30	6.70	6.65	6.60	6.40	22.50	22.58	22.66	22.96
C	0.30	9.00	8.00	7.40	6.80	18.36	20.06	21.02	21.92
A	0.11	7.80	7.20	6.90	6.60	20.52	21.54	22.02	22.47
B	0.11	6.70	6.70	6.60	6.40	22.50	22.50	22.66	22.96
C	0.11	7.20	6.70	6.40	6.10	21.60	22.45	22.93	23.38
A	0.035	7.10	6.60	6.50	6.30	21.78	22.67	22.79	23.09
B	0.035	6.60	6.40	6.30	6.20	22.68	23.02	23.18	23.33
C	0.035	6.70	6.30	6.10	5.80	22.50	23.18	23.50	23.95
A	Blank	19.2	19.1	19.0	18.9	.....	.....	.....	.....
C	Blank	18.9	18.7	18.5	18.4	.....	.....	.....	.....

* Carrying a constant of 24.1 m.e. of SiO_2.

† Continuous agitation, without any attrition agent.

‡ Continuous agitation with one hundred ½-inch steel balls.

§ Continuous agitation with 25 gm. of purified sea sand.

ground quartz and gel A, after ignition at 600° and at 900°C. The 200-mesh quartz showed a very active Brownian movement under the microscope. A considerable fraction of the pulverulent quartz was less than 0.001 mm. in diameter and would be designated as colloidal under the definition adopted by soil investigators.

The results of these experiments are given in table 3. The data in the last column of that table give the absorptions registered by the different materials on the basis of equivalents of $Ca(OH)_2$ absorbed by each equivalent of SiO_2.

If the decimal point be shifted two places to the right the figures may be made to read as the percentage of the absorption that would be required by the $Ca(OH)_2$:SiO_2 ratio of 1:1. These results indicate that the degree of hydra-

TABLE 3

Speed and extent of $Ca(OH)_2$ absorption by silica gels of different degrees of hydration

SILICEOUS MATERIAL	H_2O CONTENT	QUANTITY USED	CONTACT PERIOD	0.1 *N* TITRATION PER 50 CC. SOLUTION	$Ca(OH)_2$ ABSORPTION	
					Per exp.	Per one equiv. SiO_2
	per cent	*gm.*	*days*	*cc.*	*m.e.*	
Ground quartz, 100 mesh	0	5.0 (178 m.e.)	0	22.0		
			5	22.0	0	0
			10	21.2	0.76	0.004
Ground quartz, <200 mesh	0.7	5.0 (178 m.e.)	0	22.0		
			5	17.8	4.20	0.024
			10	16.0	5.91	0.032
Prepared silica, gel A	26.2	1.0 (244 m.e.)	0	18.2		
			5	4.8	24.1	0.98
			10	4.8	24.1	0.98
Silicic acid "C.P."	26.0	1.0 (24.5 m.e.)	0	18.2		
			5	4.4	24.8	1.01
			10	4.1	25.4	1.03
Prepared silica, gel B	56.15	1.5 (21.9 m.e.)	0	19.2		
			2	6.7	22.9	1.04
			5	6.6	23.0	1.05
"Glaucosil"—by-product of potash extraction from Glauconite*	9.4	1.0 (28.2 m.e.)	0			
			5	2.8	27.7	0.98
			10	2.4	28.4	1.01
Silica gel A, heated about 600°C. for 2 hours	0.7	0.5 (12 m.e.)	0	19.2		
			5	14.5	8.96	0.71
			10	12.4	12.53	1.00
Silica gel A, heated at about 900°C. for 2 hours	0	0.5 (12.2 m.e.)	0	19.2		
			5	18.5	1.26	0.10
			10	17.6	2.79	0.22

* Obtained from U. S. Bureau of Chemistry and Soils through courtesy of Mr. Jacob.

tion of a silica gel does not influence its capacity to absorb $Ca(OH)_2$ from solution. The five gels show a range of from 0.7 per cent to 56.15 per cent in water content, yet all show an absorption that approximates a CaO to SiO_2 ratio of 1:1. After the hydrated gel A had been heated to 600°C. its absorptive

capacity was impaired only slightly, as is shown by the respective values of 0.71 and 0.98 for the 5-day period. The ignition at 900°C., however, reduced the activity of the silica considerably, though not beyond recovery. It may be that the heating was not merely a simple dehydration, and that some crystallization of the SiO_2 took place. It should be borne in mind that the ground quartz was not only anhydrous, but also of crystalline nature. The latter property, rather than either degree of hydration or surface, probably explains the meager absorptive capacity of the quartz. The absorption effected by the 100-mesh is only about 2 to 3 per cent of that shown by a normal gel. This absorption may measure very closely the actual colloid content of the quartz sample.

It may be concluded, therefore, that dehydration without structural or constitutional changes, has no effect upon the capacity of silica to absorb $Ca(OH)_2$ from solution.

THE INFLUENCE OF $Ca(OH)_2$ CONCENTRATION UPON CaO-SiO_2 ABSORPTION EQUILIBRIA

The influence of $Ca(OH)_2$ concentration upon absorption equilibria was studied with different kinds of hydrated gels. Little is known regarding the nature of this absorption and the composition of the products that result from different conditions of $Ca(OH)_2$ concentration. It is possible that both chemical reaction and absorption take place at different stages of the process. It was sought to determine whether the absorption of $Ca(OH)_2$ from solution by the silica follows the so-called Freundlich absorption isotherm, which is generally taken as characteristic of a surface absorption, or whether another type of curve would be obtained to suggest a different interpretation.

Experiments with silica gel A

In this experiment, 1-gm. charges of gel A were used after it had been ground to a fineness of 200-mesh. Calcium oxide was used in charges of 1-gm. up to 1.75 gm., with 0.125-gm. progressions in a constant volume of 900 cc. of freshly-distilled water. Agitation with one hundred $\frac{1}{8}$-inch steel balls was continued for 5-, 10-, and 15-day periods and alkalinity determinations were made at the end of each of those periods to determine the $Ca(OH)_2$ absorptions. Because of the presence of solid $Ca(OH)_2$ the initial concentration of $Ca(OH)_2$ could not be determined by direct titration, except for the smallest addition. These values were computed from the 1 gm. titration value by proportion.

When graphed (fig. 1), the data of table 4 show that the absorption of $Ca(OH)_2$ by the silica is affected by the final hydroxide concentration. The configuration obtained conforms to an absorption curve that is expressible by the Freundlich absorption equation; that is, $x = a \cdot C^{\frac{1}{n}}$, in which x is the absorption of $Ca(OH)_2$, C is the final concentration and a and n are constants to be

determined experimentally. The computation of these constants, however, will be deferred till the constancy of the equilibria data is made more certain.

The periodic data in table 4 show that the major part of the absorption took place during the first 5 days of contact. Only small decreases in concentration and increases in absorption were noted after that period. It makes considerable difference in the final results whether the small absorption values after the first period are disregarded or included in the main data. A part of the continued absorption of $Ca(OH)_2$ is undoubtedly due to the action of the lime water upon the glass container. But it would be unsafe to assume that all of the continued absorption is thus to be accounted for. Supplemental experi-

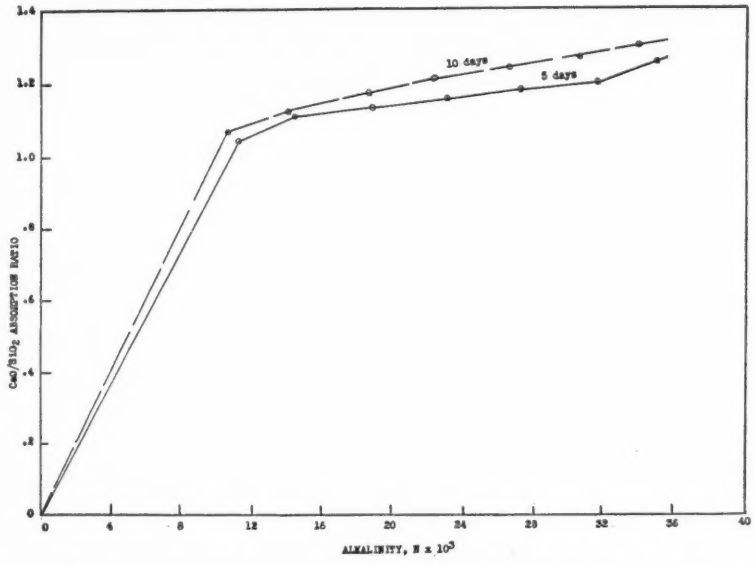

FIG. 1. EFFECT OF EQUILIBRIUM ALKALINITIES UPON $Ca(OH)_2$ ABSORPTION BY SILICA HYDROGEL A

ments relative to the action of $Ca(OH)_2$ solution on the glass containers will be referred to in detail later. These experiments demonstrate the difficulty of applying a uniform correction for blanks.

Experiments with silica gel B

This gel was more hydrated than the gel used in the preceding experiment; it contained 56 per cent H_2O, whereas gel A contained only 26 per cent. Charges of 1.5 gm. of a 100-200-mesh product were used. The CaO additions extended over a greater range and these were so calculated as to give a number of experimental points at lower equilibrium concentrations than those obtained pre-

viously. The distilled water constant, the use of steel balls, and the titrations and method of computations were all the same as those described in the previous experiments.

TABLE 4

Effect of varying $Ca(OH)_2$ concentrations upon the absorption of $Ca(OH)_2$ by silica gel A during different periods of contact†

EXPERIMENT NUMBER	CaO ADDED	0.1 *N* TITER PER 50 CC. OF SOLUTION				ABSORPTION OF $Ca(OH)_2$, AS COMPUTED FROM DECREASE IN CONCENTRATION					
		Initial	At the end of			Per gram of gel after			$CaO:SiO_2$ ratio after		
			5 days	10 days	15 days	5 days	10 days	15 days	5 days	10 days	15 days
	gm.	*cc.*	*cc.*	*cc.*	*cc.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
123	1.000	19.50	5.70	5.40	5.30	24.84	25.39	25.55	1.031	1.053	1.060
124	1.125	21.98*	7.30	7.10	6.90	26.42	26.76	27.08	1.096	1.110	1.123
125	1.250	24.46*	9.50	8.90	8.60	26.93	27.95	28.43	1.117	1.160	1.180
126	1.375	26.94*	11.60	10.80	10.60	27.61	28.97	29.29	1.146	1.202	1.215
127	1.500	29.42*	13.70	12.90	12.50	28.30	29.66	30.30	1.174	1.231	1.257
128	1.625	31.90*	15.80	14.90	14.60	28.98	30.51	30.99	1.202	1.258	1.286
129	1.750	34.38*	17.60	17.10	16.80	30.20	31.05	31.53	1.253	1.288	1.308

* Computed from the value of 1-gm. CaO blank.

† One-gram charges of silica gel and 900 cc. of distilled water were used in all experiments.

TABLE 5

Effect of varying $Ca(OH)_2$ concentrations upon the absorption of $Ca(OH)_2$ by freshly prepared, air-dried, 100-mesh silica gel B

EXPERIMENT NUMBER	CaO ADDITION*	0.1 *N* TITER PER 50 CC. AFTER					ABSORPTION OF $Ca(OH)_2$ AT CONTACT PERIODS OF				$CaO:SiO_2$ ABSORPTION RATIO AFTER			
		0 day	2 days	5 days	10 days	15 days	2 days	5 days	10 days	15 days	2 days	5 days	10 days	15 days
	gm.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*				
272	0.250	4.70	2.0	1.9	1.8	1.7	4.86	5.03	5.23	5.53	0.22	0.23	0.24	0.26
273	0.500	9.60	1.5	1.5	1.5	1.6	14.58	14.58	14.58	14.58	0.67	0.67	0.67	0.67
274	0.750	14.5	3.3	3.2	2.3	1.8	20.16	20.33	21.77	22.52	0.92	0.93	0.99	1.03
275	0.875	16.95	4.9	4.6	3.9	3.4	21.69	22.20	23.32	24.07	0.99	1.01	1.07	1.10
276	1.000	19.40	6.7	6.6	6.1	5.7	22.86	23.03	23.83	24.43	1.04	1.05	1.09	1.12
277	1.125	21.85	8.5	8.3	6.9	6.1	24.03	24.37	26.61	27.81	1.10	1.11	1.22	1.26
278	1.250	24.30	10.6	10.1	9.2	8.6	24.66	25.51	26.95	27.85	1.13	1.16	1.23	1.28
279	1.375	26.75	12.6	12.2	11.5	10.9	25.47	26.15	27.37	28.27	1.16	1.19	1.25	1.30
280	1.500	29.20	14.6	14.3	13.6	13.1	26.28	26.79	27.91	28.66	1.20	1.22	1.28	1.30
281	1.625	31.65	16.7	16.3	15.5	14.7	26.91	27.59	28.97	30.17	1.23	1.26	1.32	1.38
282	1.750	34.10	17.8	18.1	18.2	17.8	(29.34)	28.83	28.67	29.27	1.34	1.32	1.32	1.34

* 1.5 gm. 100–200 mesh gel containing 21.7 m.e. SiO_2 was also added.

The results of this experiment are presented in table 5 and graphed in figure 2. They confirm the main features of the preceding experiment relative to configuration of the absorption curves and the continued shifting of equilibria

during extended contact. The change between the 2-day and 5-day periods is not great, but the subsequent changes are much greater and somewhat erratic. The breaking up of the continuity in the curves at the 10- and 15- day periods might be taken as further proof that the additional absorptions were due to extraneous causes and not to the silica charges. The outstanding feature of this experiment, however, is the apparent displacement of the first experimental point in the main outline of the curve. As shown by the data of table 5, an alkalinity of 0.004 *N* resulted from the addition of 0.25 gm. CaO to 900 cc. H_2O in which there was a suspension of 21.7 milliequivalent of SiO_2

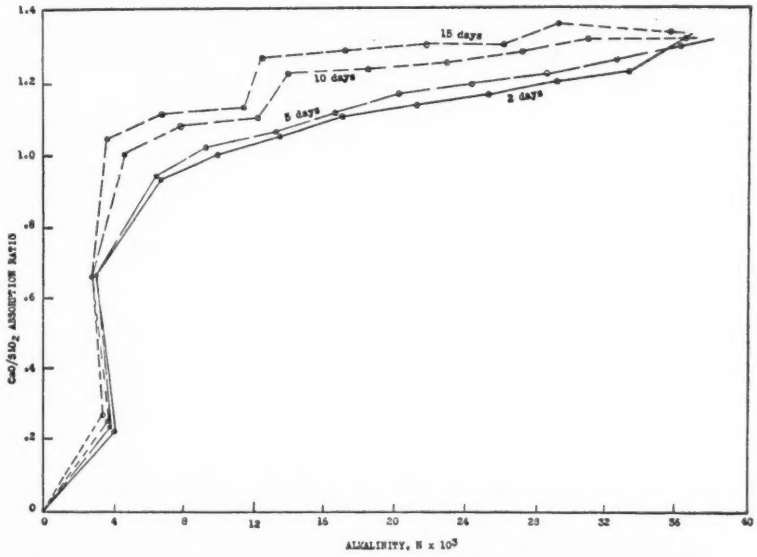

FIG. 2. EFFECT OF EQUILIBRIUM ALKALINITIES UPON $Ca(OH)_2$ ABSORPTION BY SILICA HYDROGEL B

gel. In accordance with the rules governing absorption equilibria, an additional increment of 0.25 gm. CaO should produce an increase in the concentration of the solute. In this experiment, however, the addition of 0.5 gm. of CaO was followed by a decrease in alkalinity as compared with the 0.25-gm. CaO addition. To eliminate the possibility of manipulative error, the two experimental points were reproduced and proved. The conclusion to be drawn from this unusual behavior is that a change in the composition of the absorption, or reaction, product has taken place at, or about, that point in the curve. This conclusion will be substantiated and amplified in a later part of this paper.

Experiments with silica hydrosol

An attempt was made to establish the absorption isotherm during a brief contact period, so that the action of the glassware might be disregarded. For this purpose a silica hydrosol was prepared by dissolving the 12-mesh silica gel B in an equivalent amount of NaOH and pouring the solution into an excess of HCl. The original SiO_2 content of the hydrosol was 11.25 gm. to a liter. The resultant mixture was then dialyzed in parchment bags for 10 days, with two changes of water daily. After dialysis, only 3.431 gm. of SiO_2 remained. Hence, approximately two-thirds of the silica diffused through the parchment during the dialysis.

A series of experiments, using this hydrosol with varying quantities of CaO and a constant of 400 cc. distilled water, was set up. The silica hydrosol was

TABLE 6

Effect of varying $Ca(OH)_2$ concentrations upon the absorption of $Ca(OH)_2$ by a dialyzed silica hydrosol

NUMBER	CaO ADDITION*	0.1 *N* TITER PER 50 CC. AFTER					ABSORPTION OF $Ca(OH)_2$ COMPUTED FROM DECREASE IN CONCENTRATION							
							Per experiment after				CaO:SiO_2 ratio after			
		0 day	2 days	5 days	10 days	15 days	2 days	5 days	10 days	15 days	2 days	5 days	10 days	15 days
	gm.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*				
264	0.50	9.60	2.3	2.1	1.9	1.9	13.14	13.48	13.80	13.80	0.45	0.46	0.47	0.47
265	0.75	14.50	1.4	1.2	1.2	1.1	23.58	23.92	23.92	24.07	0.80	0.80	0.81	0.82
266	1.00	19.40	3.7	3.6	3.5	3.4	28.26	28.43	28.59	28.74	0.96	0.96	0.97	0.97
267	1.25	24.30	6.7	6.7	6.5	6.5	31.68	31.68	32.00	32.00	1.07	1.07	1.08	1.08
268	1.50	29.20	10.3	10.1	9.8	9.5	34.02	34.36	34.84	35.29	1.15	1.16	1.18	1.20
269	1.75	34.10	14.1	14.0	13.7	13.5	36.00	36.17	36.65	36.95	1.22	1.23	1.24	1.25
270	2.00	39.00	18.1	17.9	17.6	17.4	37.62	37.96	37.96	38.74	1.28	1.29	1.30	1.31
271	2.25	43.90	19.4	19.7	20.0	19.7	.....	.....	.....	.....	....	....	....	....

* 200 cc. hydrosol containing 29.5 m.e. SiO_2 was also added.

diluted 1 to 1, and 400-cc. aliquots containing 29.5 milliequivalents of SiO_2 were added to the 400-cc. $Ca(OH)_2$ solution-suspension, with shaking. The 100 cc. distilled water used for rinsing the measuring flask was also added, making the total volume 900 cc. The $Ca(OH)_2$-silica solutions were agitated on a shaking machine *without* any attrition agent for 2-day and 5-day periods. Except for the first two or three experiments the solids settled out and gave clear supernatants in one hour; whereas all mixtures had settled completely after overnight standing. The settling volume of the precipitate increased regularly with the increase in CaO addition. The volume range was from 50 cc. to about 300 cc. after 16 hours of settling.

From the data of this experiment, as given in table 6 and in figure 3, it appears that, even when the silica is in the hydrosol state, slow increases in

absorption of $Ca(OH)_2$ occur after the first 2-day period. The total increase between the initial 2-day and the final 15-day period amounts to about 2 per cent of the total absorption. This increase may safely be attributed to the action of the $Ca(OH)_2$ solution on the flasks during the 13-day period and may be considered as inconsequential on the principal features of the experiment.

The curve of figure 3 reproduces the break that was observed in the curve given in figure 2 from the preceding experiment with gel B. It is evident that the observed absorption is not a single-valued function of the concentration, as would be expected from the absorption equation. By following the abscissae between the vertical broken lines in figure 3, we find not only that the curve is

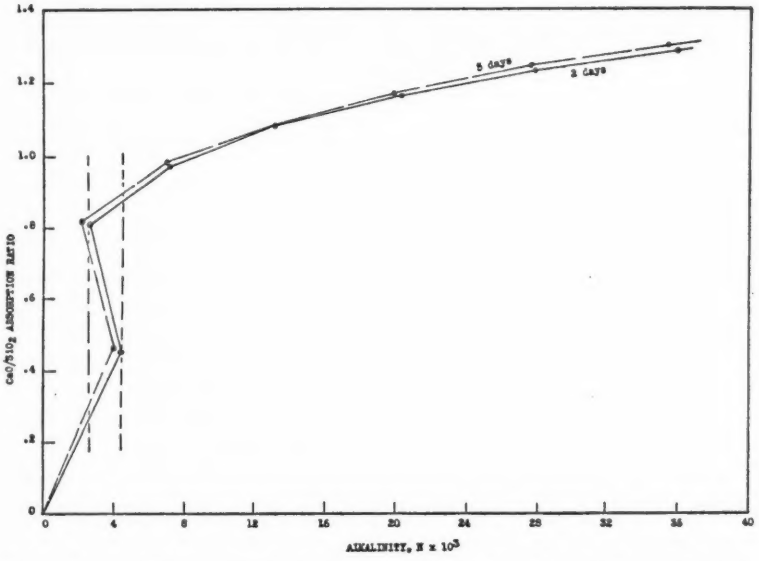

FIG. 3. EFFECT OF EQUILIBRIUM ALKALINITIES UPON $Ca(OH)_2$ BY DIALIZED SILICA HYDROSOL

discontinuous, but also that every alkali concentration between the two lines supplies three absorption values, two of which are very widely separated from each other. The fact that the Freundlich absorption equation is inapplicable in our experiment at concentrations below 0.005 N is less important than the circumstances which point to the chemical reactions between silica gel and $Ca(OH)_2$ at great dilutions and to the evidence of change in the solid-phase components of the system induced by small increases in the imposed CaO/SiO_2 ratio. This feature will be examined in detail further. The immediate object was to establish the absorption isotherm over an operative range of concentration, and to establish a formula that would serve as a measure in future work. It may be noted that the operation of the Freundlich equation in a certain

absorption process does not preclude the possibility of simultaneous chemical action. It will be shown later that the present studies furnish an example of a series of superimposed chemical reactions that culminate in an absorption process.

COMPUTATION AND TESTING OF $Ca(OH)_2$-SiO_2 ABSORPTION CONSTANTS

The first test for the range of applicability of the absorption equation $x = a.C^{\frac{1}{n}}$ was to plot the logarithms of the absorptions against the logarithms of the concentrations, by using the experimental data from table 6 to obtain the curve of figure 4. It will be observed that the points lie closely enough to a straight line to make the absorption equation applicable for the data presented.

The evaluation of the constants n and a was next considered. A series of equations: $\log X = \log a + \frac{1}{n} \log C$, based on the experimental data, was set up. Eliminating $\log a$ by subtraction of one equation from the next one, we obtain for n an average value of 5.5, or 0.1818 for $\frac{1}{n}$. By the substitution of this value for $\frac{1}{n}$ in the foregoing equation the average value of 2.34 was obtained for the constant a. The equation then assumes the definite expression of $x = 2.34\ C^{0.1818}$, or, converting into logarithmic form, $\log X = \log 2.34 + 0.1818 \log C$.

The experimental data used to obtain the curve of figure 4 show agreement with the calculated values within less than one per cent of the total absorption, and validate the absorption formula for the $Ca(OH)_2$-silica-gel system within the alkalinity-concentration range of 0.005 N and above.

The absorption formula may then be utilized as a basis of comparison relative to the attainment of equilibria at a given period of contact, as found in the preceding experiments. Such a comparison of the determined and computed absorption values for the gels A and B and the hydrosol is given in table 7.

A good agreement between the determined and calculated values was obtained in the 5-day absorption data for both gel B and the silica hydrosol. The absorption data for gel A which was the least hydrated of the three gels used falls from 2 to 4 per cent short of the calculated values. Because of the great difference in the degree of hydration, the agreement between the absorption data may be considered satisfactory. Apparently, there was a continued and unexplained absorption above the calculated values after the 5-day period. To determine that this was not due to an equilibrium shift by the silica, a supplemental experiment was carried out.

THE STABILITY OF THE ABSORPTION EQUILIBRIA

This experiment was planned to determine whether the continued absorption, previously noted, was due to reaction of the calcium hydroxide on the added

silica or on the flasks. Charges of 1.5, 3.0, 4.5, and 6.0 gm. of 35-mesh silica, gel B, were agitated with steel balls and CaO additions that gave a constant excess of alkali, as established by previous experiments. The data for the 2-, 5-, 12-, and 15-day contact periods are given in table 8.

If the continued absorptions were due solely to reactions within the system, the titration decreases and the absorption increments after the first period

TABLE 7

A comparison between the calculated and the experimentally determined absorption capacities of silica of different degrees of hydration, after 5-day's contact

SILICA GEL A			SILICA GEL B			SILICA HYDROSOL		
Concentration $N \times 10^3$	Absorption		Concentration $N \times 10^3$	Absorption		Concentration $N \times 10^3$	Absorption	
	Calculated	Found		Calculated	Found		Calculated	Found
11.4	1.04	1.03	6.4	0.93	0.93	....	....	....
14.6	1.08	1.10	9.2	1.00	1.01	7.2	1.95	0.96
19.0	1.04	1.12	13.2	1.07	1.05	13.4	1.05	1.07
23.2	1.18	1.15	16.6	1.11	1.11	20.2	1.15	1.16
27.4	1.21	1.17	20.2	1.15	1.16	28.0	1.22	1.23
31.6	1.25	1.20	24.4	1.19	1.19	35.8	1.28	1.29
35.2	1.27	1.25	28.6	1.23	1.22	....	....	....
....	....	....	32.6	1.26	1.26	....	....	....

TABLE 8

Effect of increasing charges of silica gel upon the stability of the CaO-SiO_2 absorption equilibria

NUMBER	SILICA ADDED		CaO ADDED	0.1 *N* TITER PER 50 CC. AFTER				ABSORPTION* OF $Ca(OH)_2$ AFTER PERIODS OF				CaO:SiO_2 ABSORPTION RATIO AFTER			
				2 days	5 days	12 days	15 days	2 days	5 days	12 days	15 days	2 days	5 days	12 days	15 days
	gm.	*m.e.*	*gm.*	*cc.*	*cc.*	*cc.*	*cc.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*				
1	1.5	20.7	1.0	6.6	6.2	5.6	5.4	22.68	23.36	24.00	24.30	1.10	1.13	1.16	1.17
2	3.0	41.4	1.651	6.6	6.1	5.4	5.2	43.36	46.21	46.69	46.99	1.10	1.12	1.13	1.14
3	4.5	62.1	2.302	6.6	6.2	5.9	5.7	68.04	68.72	69.20	69.50	1.10	1.11	1.11	1.11
4	6.0	82.8	2.953	6.6	6.3	6.1	6.1	90.72	91.23	91.55	91.55	1.10	1.10	1.11	1.11

* Calculated from the average blank, values of:
19.2 cc. 0.1 *N* for 50 cc. from first gram CaO.
19.5 cc. 0.1 *N* for every additional gram of CaO.
12.6 cc. 0.1 *N* for every additional 0.651 gm. CaO.

should be approximately twice, three times, and four times as great in nos. 2, 3, and 4, respectively, as in no. 1. On the other hand, if continued absorption was due to an attack on the surface of the flask, the periodic increases would be uniform and not in proportion to the amount of added silica. The data of table 8 demonstrate that the absorption after the 2-day period is not proportionate to the silica charge. The logical conclusion is that the small and con-

tinued absorption of $Ca(OH)_2$ in this experiment and all previous experiments, is due to a slow and varying attack of the limewater on the glass. Mixtures 1, 2, and 3 were again sampled after 6 weeks further standing and occasional agitation. The decreases in the titrations, expressed as cubic centimeters of 0.1 normality per 50 cc., were found to be 1.3, 1.5, and 1.33, respectively. This affords further confirmation of the correctness of the above observations.

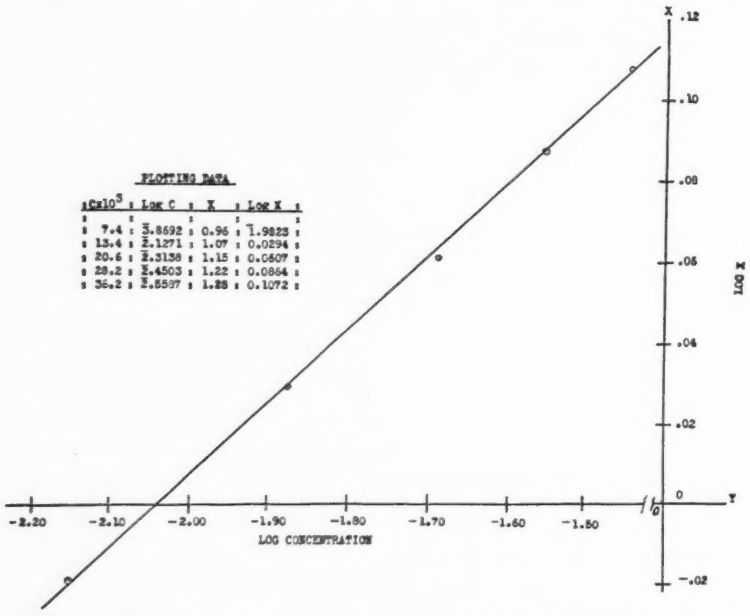

FIG. 4. LOGARITHMIC PLOT OF CONCENTRATION-ABSORPTION DATA TO TEST APPLICABILITY OF FREUNDLICH ABSORPTION EQUATION

The several experiments and observations on the effect of $Ca(OH)_2$ concentration upon the CaO-SiO_2 absorption equilibrium may be summarized as follows:

The absorption of $Ca(OH)_2$ by hydrated silica occurs in accordance with the Freundlich absorption isotherm, when the final concentrations of $Ca(OH)_2$ are above 0.005 N.

When the final concentrations are less than 0.005 N, several inflections appear in the absorption curve and these point to a series of chemical combinations between the $Ca(OH)_2$ and the SiO_2.

The formula $x = 2.34\ C^{.1818}$ has been computed to express the $Ca(OH)_2$-SiO_2 absorption equilibria. This formula holds within approximately one per cent of the total absorptions, during the 5-day contact period, in all experiments except those with the less hydrated silica A, in which case the values were about 3 per cent low.

The slow but definite shift in absorption equilibria after the first 2- or 5-day contact was found to be due entirely to the action of the hydroxide upon the glass containers.

Special consideration is required to determine the nature of the chemical reactions that occur over the entire range of concentrations.

COMMON- AND VARIANT-ION EFFECT UPON THE $Ca(OH)_2$-SiO_2 ABSORPTION EQUILIBRIA

The absorption constants previously deduced were computed on the basis of pure $Ca(OH)_2$ in solution and pure SiO_2 as the absorbent. If the formula is to be extended to a study of the decomposible silicates of calcium and the alkalies, it becomes necessary to determine to what extent the presence of neutral salts and the hydroxides of the respective bases may affect the established $Ca(OH)_2$-SiO_2 absorption equilibria.

TABLE 9

The effect of $CaCl_2$ concentrations upon the $Ca(OH)_2$—SiO_2 absorption equilibria during 48-hours of contact

$CaCl_2$ ADDITIONS		0.1 *N* TITER PER 50 CC.			$Ca(OH)_2$ ABSORB-TION	$Ca(OH)_2/SiO_2$ RATIO		
Quantity	Normality	A-Blanks	B-Exp.	A—B		Found	Theoretical	Deviation from theoretical
gm.					*m.e.*			
None	0	14.5	3.3	11.2	20.2	0.92	0.94	−0.02
0.4995	0.01	14.5	3.0	11.5	20.7	0.95	0.92	+0.03
2.4975	0.05	14.5	2.8	11.7	21.1	0.96	0.91	+0.05
4.9950	0.10	14.5	2.6	11.9	21.4	0.98	0.90	+0.08
12.4880	0.25	14.5	2.6	11.9	21.4	0.98	0.90	+0.08

EFFECT OF A NEUTRAL CALCIUM SALT

In this experiment a 1.5-gm. constant of silica gel B, 100–200-mesh, containing 21.9 m.e. of SiO_2, was used, together with 0.75 gm. CaO in 900 cc. of water. Calcium chloride was added in graded quantities to give concentrations varying from 0 to 0.25 *N*. A series of blanks was run to include all the reagents other than silica. After agitation and overnight settling, the alkalinities of the blanks and mixtures were determined and the $Ca(OH)_2$ absorptions were computed in terms of milliequivalents. The total $Ca(OH)_2$ absorptions were divided by the milliequivalents of SiO_2 to obtain the $Ca(OH)_2$-SiO_2 absorption ratios. The theoretical $Ca(OH)_2$-SiO_2 absorption ratios were computed from the equilibrium alkalinities according to the formula $x = 2.34\,C^{0.1818}$.

From the data of table 9 it will be seen that the addition of $CaCl_2$ caused enhancements in the $Ca(OH)_2$ absorptions from 3 to 6 per cent within the prescribed range of $CaCl_2$ concentrations. When compared with the theoret-

ical absorption ratios, which take into consideration also the decreased alkalinities, the absorption increases are from 3 to 10 per cent greater. These figures may be taken as indicative of the general trend of the $CaCl_2$ effect solely within the range of the concentrations that were imposed. Other figures would undoubtedly obtain if the equilibria alkalinities were materially different from those imposed.

Effect of a neutral alkali salt

The procedure carried out in the preceding experiment was duplicated with additions of NaCl instead of $CaCl_2$. After 48-hours agitation the absorption of $Ca(OH)_2$ was determined and compared with the theoretical values for $Ca(OH)_2$ and SiO_2 only. The data of table 10 show that 0.01 to 0.50 *N* concentrations of NaCl cause a repression of 0.4 to 1.8 m.e. $Ca(OH)_2$ in CaO

TABLE 10

Effect of NaCl upon the absorption of $Ca(OH)_2$ by 100–200 mesh silica gel during 48-hour's agitation

NUMBER	NaCl ADDED		CaO ADDITION	SILICA ADDITION	0.1 *N* TITER PER 50 CC.	ABSORPTION OF $Ca(OH)_2$	$Ca(OH)_2/SiO_2$ RATIO		
	Quantity	Normality					Found	Calculated by formula	Deviation from theoretical
	gm.		*gm.*	*gm.*	*cc.*	*m.e.*			
1	None	0	1.0	1.5	6.7	22.5	1.03	1.07	−0.04
2	0.5265	0.01	1.0	1.5	6.9	22.1	1.01	1.07	−0.06
3	1.316	0.05	1.0	1.5	7.1	21.8	1.00	1.08	−0.08
4	5.265	0.10	1.0	1.5	7.3	21.4	0.98	1.09	−0.11
5	13.163	0.25	1.0	1.5	7.6	20.9	0.95	1.09	−0.14
6	26.325	0.50	1.0	1.5	7.7	20.7	0.95	1.10	−0.15
Blank	26.325	0.50	1.0	None	19.2	....	....	....	....
Blank	None	0	1.0	None	19.2	....	....	....	....

absorption, with a maximum decrease of approximately 8 per cent. When compared with the theoretical values, the absorption ratio shows still greater decreases resultant from NaCl. Although the control experiment shows a deficiency of 4 per cent from the theoretical value, the experiments with NaCl show deviations of 6 to 15 per cent, depending upon the concentration of NaCl.

These observations relative to the effect of NaCl were responsible for a more detailed study, in which silica hydrosol was used. Two series of standard sodium silicate solutions were made up. In series A, the SiO_2 was dissolved in one equivalent of NaOH. In series B, two equivalents of NaOH were used. Standard HCl was used in quantities required to neutralize NaOH equivalences of the sodium silicate solutions. The aliquot of each silica solution contained 25 m.e. of SiO_2. The NaCl concentration in series A was 0.0275 *N*, whereas that in series B was 0.055 *N*. Different quantities of CaO were added in each series

to establish the effect of NaCl on the absorption equilibrium over a wide range of $Ca(OH)_2$ concentration. The residual alkalinities determined after the 16-hour-contact period were found to be practically identical with corresponding values that were determined after 3 days.

TABLE 11

The effect exerted by NaCl upon the absorption of $Ca(OH)_2$ by silica hydrosol

EXPERIMENT NUMBER	CaO ADDITION	0.1 *N* TITER PER 50 CC.		$Ca(OH)_2$ ABSORBED	CaO/SiO_2 ABSORPTION RATIO		
		Initial	After 16 hours		Found	Calculated	Deviation due to NaCl
	gm.	*cc.*	*cc.*	*m.e.*			
A. 25 m.e. SiO_2 in 0.028 N NaCl solution							
202	0.500	9.15	2.60	11.79	0.47	(0.90)	....
203	0.750	14.00	2.10	21.42	0.86	0.86	0
204	1.000	18.90	5.10	24.84	0.99	1.01	−0.02
205	1.250	23.80	8.70	27.18	1.09	1.12	−0.03
206	1.375	26.25	10.60	28.17	1.13	1.16	−0.03
207	1.500	28.70	12.50	29.16	1.17	1.20	−0.03
208	1.625	31.15	14.60	29.79	1.19	1.23	−0.04
209	1.750	33.60	16.60	30.60	1.22	1.26	−0.04
210	1.875	36.05	18.70	31.23	1.25	1.29	−0.04
211	0.50	.....	9.15	.....	....	....	....
212	0.75	.....	14.00	.....	....	....	....
213	1.00	.....	18.90	.....	....	....	....
B. 25 m.e. SiO_2 in 0.055 N NaCl solution							
214	0.500	8.85	2.80	10.89	0.44	(0.91)	....
215	0.750	13.70	2.00	21.06	0.84	(0.86)	−0.02
216	1.000	18.60	5.10	24.30	0.97	1.01	−0.04
217	1.250	23.50	8.50	27.00	1.08	1.11	−0.03
218	1.375	25.95	10.60	27.63	1.11	1.16	−0.05
219	1.500	28.40	12.40	28.80	1.15	1.20	−0.05
220	1.625	30.85	14.40	29.61	1.18	1.23	−0.05
221	1.750	33.30	16.40	30.42	1.22	1.26	−0.06
222	1.875	35.75	18.60	30.87	1.23	1.29	−0.06
223	0.500	.....	8.85	.....	....	....	....
224	0.750	.....	13.70	.....	....	....	....
225	1.000	.....	18.60	.....	....	....	....

The data for the 16-hour period (table 11) show that the effect of NaCl on the $Ca(OH)_2$-SiO_2 absorption varies not only with the concentration of NaCl but also with the equilibrium alkalinity of the experiment. Comparisons between the experiments of series A and the corresponding experiments of series B show that the additional NaCl in series B caused a constant decrease of 0.02 units in the absorption ratios. The effect of the same NaCl concentration with increasing equilibria alkalinities in each series was to depress the absorption

ratio. The uniformity of the NaCl effect suggests that a correction on the $Ca(OH)_2$-SiO_2 absorption equilibrium equation might easily be applied to take care of the deviation caused by the presence of NaCl in solution. These findings might be applied in evolving a laboratory routine for the approximate determination of the SiO_2 content of sodium silicate solutions and silica melts in general.

EFFECT PRODUCED BY AN ALKALI HYDROXIDE

In this experiment, 1.5-gm. charges of a silica gel of 100–200-mesh, 0.75 gm. of CaO, and 900 cc. of water were used as constants. Sodium hydroxide was added in sufficient quantities to give NaOH normalities of 0.007, 0.014, and 0.028. The titrations, absorption data, and deviations due to concentrations of NaOH are given in table 12. These data show that sodium hydroxide exerted a decidedly depressive effect on the absorption of $Ca(OH)_2$. A NaOH

TABLE 12

*Effect of NaOH concentrations upon the $Ca(OH)_2$—SiO_2 absorption equilibria**

EXPERIMENT NUMBER	SiO_2 USED	NaOH ADDED		0.1 *N* TITER PER 50 CC.			$Ca(OH)_2$ ABSORPTION	CaO/SiO_2 ABSORPTION RATIO		
		0.25 N	Final concentration	Initial	After 2 days	Decrease		Found	Theoretical	Deviation due to NaOH
	m.e.	*cc.*	*N*	*cc.*	*cc.*	*cc.*	*m.e.*			
290	None	None	0	14.4	14.4	0	0	....	....	....
291	None	25	0.007	17.7	17.7	0	0	....	....	....
292	21.9	25	0.007	17.7	6.2	11.5	20.7	0.95	1.05	−0.10
293	21.9	50	0.014	21.0	9.1	11.9	21.4	0.98	1.13	−0.15
294	21.9	100	0.028	27.6	15.3	12.3	22.1	1.01	1.24	−0.23

* A 1.5-gm. constant of 100–200 mesh silica gel was used.

concentration between 0.01 and 0.02 *N* was sufficient to produce a depression of from 15 to 20 per cent in the CaO absorption.

The difference in the effects of the neutral alkali salt and alkali hydroxide is very strikingly demonstrated by the results of the two preceding experiments. In conducting $Ca(OH)_2$ absorption studies, it would seem imperative to insure the absence of alkali hydroxides from the suspension.

The foregoing experiments on the effect of extraneous ions on the $Ca(OH)_2$-SiO_2 absorption equilibrium indicate the following:

Neutral calcium chloride caused a positive shift in the equilibrium and apparently decreased the solubility of the silicate precipitate.

Sodium chloride caused an appreciable reversion in the equilibrium, probably through the formation of soluble sodium silicates, for which a correction may be applied.

In the concentrations used, NaOH caused a marked decrease in the absorption of CaO, and its effect precludes the correct computation of the $Ca(OH)_2$-SiO_2 absorption equilibria.

CHEMICAL CHANGES INVOLVED IN THE ABSORPTION OF $Ca(OH)_2$ BY SILICA GEL

Attention has been called in this paper to the irregularities in the absorption curve at alkalinity ranges below 0.005 *N*. The probability of a series of chemical reactions was inferred from the configuration of the absorption curve. The data on this point, however, were inadequate to explain the postulated chemical changes. A further series of experiments was planned to elucidate this point.

A constant charge of 1 gm. of gel B of 200-mesh fineness was used. The aqueous $Ca(OH)_2$ solutions of 1 liter each were made up by diluting a saturated solution 1/20, 2/20, 3/20, etc. to 1/2 saturation. After the solutions were agitated and allowed to stand overnight, 50-cc. aliquots were withdrawn and titrated, ieaving 950 cc. $Ca(OH)_2$ solution of varying strengths to react with

TABLE 13

Effect of fractional CaO/SiO_2 ratios upon alkalinity values and apparent absorption of $Ca(OH)_2$ by 200-mesh silica gel

EXPERIMENT NUMBER	$Ca(OH)_2$ ADDITION		0.1 *N* TITRATION VALUE PER 50 CC.				APPARENT $Ca(OH)_2$ ABSORPTION AFTER CONTACT OF			APPARENT CaO/SiO_2 ABSORPTION RATIO × 100 AFTER		
	Milli-equivalent	CaO/SiO_2 ratio	Initial	After contact of			5 days	10 days	13 days	5 days	10 days	13 days
				5 days	10 days	13 days						
			cc.	*cc.*		*cc.*	*m.e.*	*m.e.*	*m.e.*			
311	1.90	0.116	1.00	0.70	0.70	0.67	0.57	0.57	0.62	3.5	3.5	3.8
312	3.99	0.245	2.10	1.60	1.50	1.48	0.95	1.13	1.16	5.8	6.9	7.0
313	6.18	0.380	3.25	1.90	1.90	1.78	2.57	2.57	2.73	15.8	15.8	16.7
314	8.17	0.501	4.30	2.10	2.10	2.04	4.18	4.18	4.28	25.7	25.7	26.2
315	10.26	0.616	5.40	2.10	2.00	1.94	6.27	6.45	6.55	38.5	39.5	40.2
316	12.35	0.757	6.50	1.60	1.50	1.47	9.31	9.49	9.54	57.2	58.2	58.5
317	14.54	0.892	7.65	1.90	1.70	1.70	10.93	11.29	11.29	67.7	70.0	70.0
318	16.63	1.020	8.75	2.40	2.20	2.04	12.07	12.43	12.70	74.0	76.2	78.0
319	18.53	1.137	9.75	2.80	2.60	2.49	13.21	13.57	13.76	81.0	83.2	84.4
320	20.52	1.259	10.80	3.50	3.20	3.14	13.87	14.41	14.51	85.1	88.4	89.0

the silica gel. The total volume of each solution was calculated so as to furnish a range of CaO/SiO_2 ratios between the minimum of about 0.1:1 and the maximum, which exceeded 1:1. Agitation was continuous for the 5-day, 10-day, and 13-day periods. The steel balls were omitted in order to minimize the action on the flasks. Under these conditions equilibrium is not assured; for the present purpose, however, approximation thereto is considered to be adequate. The absorptions were computed from the decrease in alkalinities after each sampling period, together with the CaO/SiO_2 absorption ratios, based on total silica charges. These data are given in table 13 and in figure 5 *a*. After the last sampling the pH values were determined by the hydrogen electrode, using a type *K* potentiometer. Hydroxyl-ion concentrations were calculateb from these data and incorporated with other data in table 14.

Aliquots of 500 cc. were withdrawn from the perfectly clear supernatant liquid, acidified with HCl, dehydrated twice, and the lime-soluble SiO_2 content was determined. The CaO content was calculated from the titration values against phenolphthalein. The residual suspensions of known volumes were acidified by the addition of 10 cc. concentrated HCl, made up to 500-cc. volumes and left undisturbed for 4 days. One-half of the clear solution was then syphoned off and analyzed for acid-soluble SiO_2. The SiO_2 found, times 2, minus the quantity of lime-soluble silica contained in the residual alkaline solution gave the total SiO_2 content of the residue that was insoluble in the lime water, but soluble in dilute acid. This technique was preferred to direct separation of the solid and liquid phases, since preliminary experiments showed that the colloidal nature of the residue precludes a satisfactory filtra-

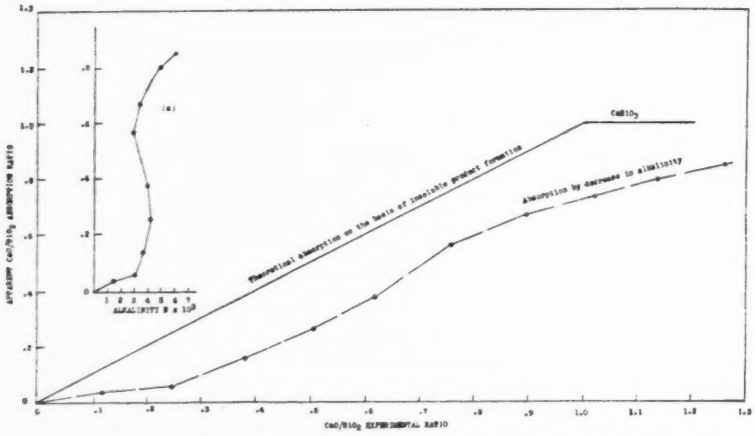

FIG. 5. EFFECT OF INCREASING EXPERIMENTAL CaO/SiO_2 RATIO AND (*a*) EFFECT OF EQUILIBRIUM ALKALINITIES UPON THE APPARENT CaO/SiO_2 ABSORPTION RATIO

tion. The SiO_2 content and the corresponding CaO content are given in table 14 under the designation "solid-phase soluble in dilute HCl." The sum of the silica found in the alkaline solution plus the acid-soluble silica is considered as the total silica that reacted in the experiment.

ABSORPTION DATA

The data that bear solely on the absorption phase of the problem and those that are presented in table 13 and figure 5 *a* will be discussed before consideration is given the relationships established by the chemical analysis. The data of table 13 show only slight increases in absorptions after the 5-day period. Although the equilibrium concentrations increased at first, then decreased, and finally showed another increase, the absorption rose steadily with each increase in the CaO/SiO_2 ratio. This further emphasizes the fact that, when below a

definite value, the final concentrations do not determine the extent of absorption. The curve *a* of figure 5 shows the same relationship between concentration and absorption that was revealed in the first 3 points in curves 2 and 3. In this case, however, the same range of concentrations is connoted by 10 experimental points and the curve is therefore much smoother and assumes the shape of an elongated *S*.

The only positive relationship that can be established by the absorption data is that brought out in the $Ca(OH)_2$ additions. This relationship may be seen in figure 5. The straight line represents an ideal condition where the absorption product would be insoluble. The determined absorptions give points uniformly below that line. The experimental curve contains several

TABLE 14

Effect of increasing CaO/SiO_2 ratios upon the composition of the solution- and the solid-phase products of the reactions

EXPERIMENT NUMBER	EXPERIMENTAL CaO/SiO₂ RATIO	ALKALINE SOLUTION-PHASE							SOLID-PHASE, SOLUBLE IN DILUTE HCl		
		Alkali-concentration $N \times 10^3$	pH value	OH-ion concentration $N \times 10^3$	Apparent degree of dissociation	CaO content	SiO_2 content	CaO/SiO_2 ratio	CaO content	SiO_2 content	CaO/SiO_2 ratio
						m.e.	*m.e.*		*m.e.*	*m.e.*	
311	0.116	1.34	9.62	0.04	0.03	1.27	5.26	1:4.14	0.63	0	.....
312	0.245	2.96	10.00	0.10	0.03	2.81	7.75	1:2.76	1.18	0	.....
313	0.380	3.56	10.53	0.34	0.09	3.38	6.52	1:1.93	2.80	0	.....
314	0.501	4.08	11.20	1.59	0.39	3.88	4.62	1:1.20	4.29	0.96	1:0.17
315	0.616	3.88	11.15	1.41	0.36	3.69	4.94	1:1.34	6.57	4.05	1:0.62
316	0.757	2.94	11.31	2.04	0.70	2.79	1.05	1:0.38	9.56	6.79	1:0.71
317	0.892	3.40	11.42	2.63	0.71	3.23	0.68	1:0.21	11.31	9.86	1:0.87
318	1.020	4.08	11.51	3.24	0.80	3.88	0.36	1:0.09	12.75	13.68	1:1.08
319	1.137	4.98	11.67	4.68	0.94	4.73	0.23	1:0.05	13.80	15.22	1:1.10
320	1.259	6.28	11.78	6.02	0.96	5.97	0.17	1:0.03	14.55	15.82	1:1.09

inflections that indicate the formation of more than one insoluble, or partially soluble, product. But a thorough understanding of the transformations that occur necessitates consideration of the chemical composition of both solution and solid phases.

COMPOSITION OF SOLUTION PHASE

The relationships between the $Ca(OH)_2$ additions and the alkalinity values found in the preceding section, indicated probable formation of soluble silicates. Consideration was therefore given to the silica that was present in the solution phase through solution by the respective alkalinities that follow cumulative additions of $Ca(OH)_2$. A conception of the changes that occur in the content of CaO and SiO_2, and in OH-ion concentration, may be gained from examination

of figure 6, where these components are expressed in normality concentrations of the equilibrium content in the solution phase, as derived from the experimental values of table 14. In considering these curves, a number of distinct transition points are observed. Of the given components—CaO, SiO_2, and OH-ions—silica appears to be most sensitive in reflecting the character of the solution. The OH-ion concentrations, and therefore the pH values, are closely coördinated with the silica content of the alkaline solutions. For every rise in the pH value, there is a corresponding drop in the silica content of the solution. The most decisive transition in the silica content of the solution takes place in the abcissae region between 6.5 and 7.5, which corresponds to OH-ion concentration change from 1.5×10^{-3} to 2.0×10^{-3}, or pH 11.2 to pH 11.3. Beginning with the pH value of 11.3, the CaO content dominates the SiO_2 content; hence, it is concluded that all higher pH values connote equilibria between $CaSiO_3$ and $Ca(OH)_2$ in different concentrations. Furthermore, beyond the pH value of 11.3 the silica content of the solutions may be considered as a solubility curve for $CaSiO_3$ in different concentrations of $Ca(OH)_2$. Moreover, the alkalinity values beyond that point may be fitted with the absorption values to follow the Freundlich absorption isotherm.

There is one possible inconsistency in these conclusions. This arises from the fact that the apparent $CaSiO_3$-$Ca(OH)_2$ equilibrium seems to be established at the experimental CaO/SiO_2 ratio of 0.75:1, that is, at a point where only 3/4 of the CaO that is required to convert all the silica to $CaSiO_3$ is present. This inconsistency might be explained by the assumption that a silicate other than $CaSiO_3$ is represented in the transition point—a silicate that conforms to the composition $3\,CaO \cdot 4SiO_2$. Although such an assumption may harmonize with the data under consideration, it would not hold when considered in the light of other facts to be brought out later. A plausible explanation of this apparent discrepancy may be supplied by the assumption that pseudo equilibrium is obtained although the full charge of the silica has not reacted with the $Ca(OH)_2$. That is, at the lower ratios of CaO/SiO_2 only the finer particles and the surfaces of the larger particles are in true equilibrium with the solution phase, and the diffusion at low concentrations is so slow that the status obtained has the appearance of true equilibrium. From this it would be expected that the transition points with reference of the pH values and SiO_2 content of solution would not differ markedly from one experiment to the next. The CaO/SiO_2 experimental ratios, with which these transitions coincide, may differ greatly, however, in accordance with the activity and size of particles of the silica gel.

Having considered the composition of the solution phase to the right of the so-called major transition region, we may well analyze briefly the area to the left of this region. The most outstanding feature in the experiments with low $CaO:SiO_2$ ratios is the decided predominance of silica over the CaO in solution. Of the first 1.90 milliequivalents of $Ca(OH)_2$ added, 1.27 remained in solution, and this effected a solution of 5.26 milliequivalents of SiO_2, which gives a ratio

of 1:4.1 for soluble CaO and SiO_2. The next addition was 3.99 milliequivalents $Ca(OH)_2$. Of this, 2.81 milliequivalents remained in solution and effected a solution of 7.75 milliequivalents SiO_2 with a CaO ratio of 1:2.8. The second addition effected the greatest solubility of SiO_2, whereas the widest CaO/SiO_2 ratio was obtained by the smallest lime addition. It is probable that small intermediate CaO additions would reveal greater silica solubility with the CaO/SiO_2 ratio of 1:4.

To ascertain the relationship between the CaO and SiO_2 present in the liquid phase, the pH values of these solutions were determined and calculated to the equivalent of OH-ion concentrations. In both of the first two solutions of table 14 the apparent degree of dissociation was found to be only 0.03; i.e., the OH-ion concentrations of the solutions were only about 3 per cent of the

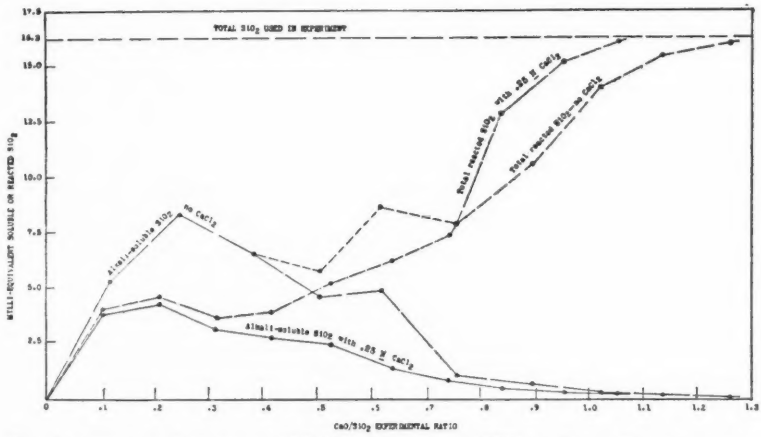
TOTAL SiO2 USED IN EXPERIMENT
Alkali-soluble SiO2 in CaCl2
Alkali-soluble SiO2 with .025 N CaCl2
Total reacted SiO2 with .025 N CaCl2
Total reacted SiO2 in CaCl2
MILLI-EQUIVALENT SOLUBLE OR REACTED SiO2
CaO/SiO2 EXPERIMENTAL RATIO

FIG. 6. EFFECT OF INCREASING CaO/SiO_2 RATIO OF $Ca(OH)_2$ TO SILICA HYDROGEL UPON TOTAL ALKALINITY, HYDROXYL ION, AND DISSOLVED SILICA

value that would obtain if all of the calcium were present as $Ca(OH)_2$, rather than in combination with SiO_2.

An increase in the CaO addition to 6.18 milliequivalents, or 38 per cent of that necessary to produce $CaSiO_3$, resulted in a decrease in the soluble silica from 7.75 to 6.52, and the CaO/SiO_2 solution ratio narrowed to 1:1.93. At the same time 2.8 milliequivalents, or nearly half of the $Ca(OH)_2$ added, was absorbed by the solid SiO_2. The pH value at this point was found to be 10.53 and the apparent degree of dissociation was calculated to be about 9.0 per cent. When the $Ca(OH)_2$ addition was raised to 8.17 milliequivalents, about half of it was absorbed by the solid SiO_2. The other half brought 4.62 milliequivalents SiO_2 into solution, which gave a CaO/SiO_2 solution ratio of 1:1.2 and caused a pH value of 11.2. Another increment of 2.15 milliequivalents of $Ca(OH)_2$ produced only slight changes in soluble CaO, silica content,

and OH-ion concentration, and all of the $Ca(OH)_2$ had been taken up by the solid phase SiO_2. From the near constancy of these values, it is apparent that we are dealing with a saturated solution of silicate whose composition corresponds very closely to the formula $3\,CaO \cdot 4SiO_2$.

The next addition of about 2 milliequivalents of $Ca(OH)_2$ caused a sudden slump in the soluble SiO_2, and an appreciable drop in alkalinity, accompanied by a rise in OH-ion concentration. The pH values show a change from 11.15 to 11.31, which corresponds to an OH-ion-concentration change from 1.41×10^{-3} to 2.04×10^{-3}, or an increase of about 45 per cent in OH-ions. This transition approaches the region that has been defined as the one for $CaSiO_3$-$Ca(OH)_2$ equilibria. A picture of the progressive changes that take place when $Ca(OH)_2$ is added in small increments to a given amount of hydrated SiO_2 from a ratio of CaO/SiO_2 0.1 to 1:1 is obtained by summarizing the above observations on the solution phase by stages, in accordance with the characteristic function of the $Ca(OH)_2$ addition:

Silica-solution stage—Characterized by dissolved $CaO:SiO_2$ ratios varying from 1:4 to 1:2; pH values ranging from 9.6 to 10.5; apparent degree of hydrolysis of 0.03 to 0.09; concentration of dissolved silica—about 0.007 *N*.

Solution—Precipitation stage—Characterized by a dissolved $CaO:SiO_2$ ratios of 1:2 to 3:4; pH values ranging from 10.5 to 11.25; apparent degree of hydrolysis about 0.36; dissolved silica from 0.0065 to 0.0050 *N*.

Precipitation stage—Characterized by dissolved $CaO:SiO_2$ ratios greatly in excess of 1 to 1; pH values above 11.25; dissolved silica from 0.001 *N* to undeterminable quantities.

COMPOSITION OF SOLID-PHASE REACTION PRODUCT

It is feasible to distinguish between the "absorption product" and the "solid-phase reaction product" as determined by the solubility of their respective silica contents in dilute HCl. Numerous qualitative tests with solid residues, in which the factors of CaO/SiO_2 ratio and time were sufficient to assure the formation of $CaSiO_3$, have shown that this product is quickly and completely dissolved by cold dilute (1 + 9) HCl. The hydrated calcium silicate of the composition $3\,CaO \cdot 4SiO_2$ was also found to be soluble in dilute acid. On the other hand, when the experimental CaO/SiO_2 ratios were inadequate to produce either of the aforementioned products the lime-silica precipitates did not yield any appreciable quantities of acid-soluble SiO_2, although considerable absorption of $Ca(OH)_2$ had taken place. No distinction can be drawn as to the solubility of the CaO content of the several residues, since all of the calcium is soluble in dilute acid.

The solubility of SiO_2 in dilute acid, as a measure for chemically combined silica, and the insolubility of the absorptively-active silica supply an interesting basis upon which to examine the data in table 14 and the curves in figure 7. It will be observed (*see* figure 5) that the absorption of $Ca(OH)_2$ by the solid-phase is manifest over the entire experimental range of CaO/SiO_2 ratios, although variant in extent. On the other hand, figure 7 shows that the acid-

soluble silica did not appear until the experimental CaO/SiO_2 ratio approached 1:2, thus coinciding with the appearance of the $3\,CaO \cdot 4SiO_2$ ratio in the acid-

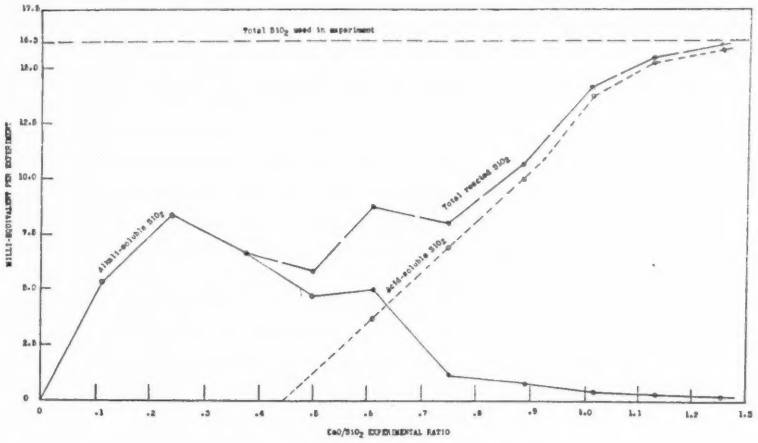

FIG. 7. EFFECT OF INCREASING CaO/SiO_2 RATIO OF $Ca(OH)_2$ TO SILICA HYDROGEL UPON SOLUTION PHASE (ALKALI-SOLUBLE) AND SOLID-PHASE (ACID-SOLUBLE) SILICA

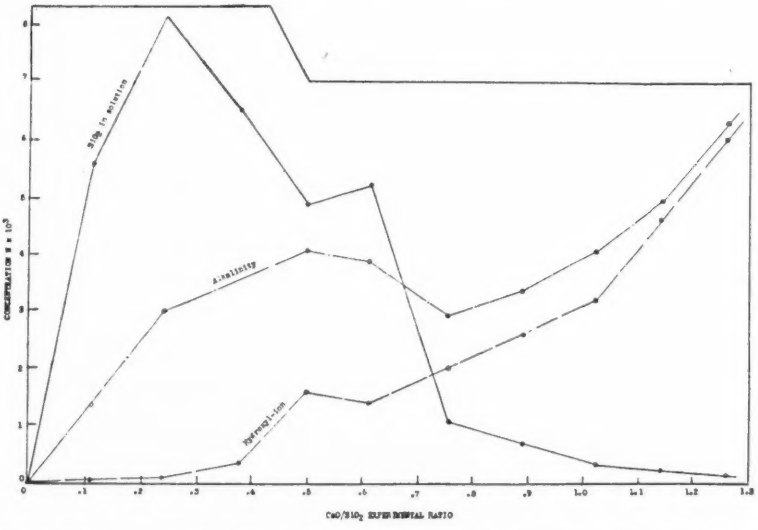

FIG. 8. EFFECT OF 0.25 *N* $CaCl_2$ UPON CALCIUM HYDROXIDE-SOLUBLE AND TOTAL REACTED SiO_2 AT DIFFERENT EXPERIMENTAL $Ca(OH)_2/SiO_2$ RATIOS

soluble product. The fact that no acid-soluble SiO_2 appears in the residue so long as the dissolved CaO/SiO_2 ratio remains 1:2, or less, may signify either

of two things. The solid products of the above CaO/SiO_2 ratios may not yield acid-soluble silica. On the other hand, the conditions of the experiment, especially the ratio of total silica to the volume of liquid, were such as to inhibit the deposition of the aforementioned solid-phase products. The correct explanation can be determined only by additional experiments.

Additions of $Ca(OH)_2$ cause a uniform increase in the acid-soluble silica when the dissolved CaO/SiO_2 ratio is changed to exceed 1:2. A comparison of the alkali-soluble and the acid-soluble silica curves in figure 7 shows that the acid-soluble lime-silica compound is in equilibrium with a soluble calcium silicate of the composition $3\ CaO \cdot 4SiO_2$ between abscissae 0.5 and 0.6. It may be assumed that the solid-phase calcium silicate in equilibrium is also of the composition $3\ CaO \cdot 4SiO_2$. The next increase in acid-soluble silica—i.e. between abscissae 0.60 and 0.75—appears to be entirely at the expense of the alkali-soluble silica. At this time, the product is in equilibrium with a calcium silicate that is only slightly soluble and which is likewise in equilibrium with an excess of lime water. In this case it may be assumed that the hydrated product $3\ CaO \cdot 4SiO_2$ has been transformed into the $CaO \cdot SiO_2$ combination. In the entire range of experimental CaO/SiO_2 ratios that produced the solid phases, we find only two hydrated silicates. One shows the composition $3\ CaO \cdot 4SiO_2$ and the other $CaO \cdot SiO_2$. Our method of attack has not disclosed the presence of a solid-phase calcium silicate of a CaO/SiO_2 ratio of 1:2, or less, to correspond to that found in the solution phase.

SUMMARY

The system $CaO\text{-}SiO_2\text{-}H_2O$ was investigated as a part of a fundamental and major study of the soil's components that react with aqueous $Ca(OH)_2$-$CaSO_4$ solutions.

The literature discloses few systematic investigations as to the nature of the reactions between $Ca(OH)_2$ and hydrated silica.

Preliminary work on the speed of $Ca(OH)_2$ absorption by silica of different origins and degrees of hydration with agitation and attrition demonstrated that:

The degree of hydration of an amorphous silica has little effect on the speed of the $CaO\text{-}SiO_2$ reaction.

The speed of the reaction, and attainment of equilibrium, decrease with increase in the size of the particles of silica gel.

Continuous agitation with ¼-inch steel balls was found to be the most expeditious procedure to induce maximum absorption with particles of 35- to 200-mesh fineness.

The abrasive action of the attrition agent on the glass containers, and the enhanced $Ca\text{-}SiO_2$ reactions thus induced, were studied.

The absorption of $Ca(OH)_2$ by hydrated silica was first investigated by the use of dialyzed silica hydrosol and two kinds of silica gels, which led to the development of the formula $x = 2.34\ C^{0.1818}$, in which x represents the molar

ratio CaO/SiO_2 in the absorption product and C the final $Ca(OH)_2$ concentration. This formula is limited in its application to equilibrium concentrations above 0.005 N.

The experiments on the reaction between $Ca(OH)_2$ and silica discolsed a series of hydrated calcium silicates of varying degree of solubility and varying CaO/SiO_2 composition ratios, whose existence is governed by the total available $Ca(OH)_2/SiO_2$ ratio and the resulting OH-ion concentration.

The solubility of their respective silica contents in dilute hydrochloric acid may be used to differentiate between the "absorption-product" and the "solid-phase reaction-product" that result from $Ca(OH)_2$-SiO_2 reactions.

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THE RESULTS OF X-RAY AND MICROSCOPICAL EXAMINATIONS OF SOIL COLLOIDS

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In 1924, W. O. Robinson and R. S. Holmes published the results of an investigation on the chemical composition of soil coilloids (7), in which they showed that a partial classification of soils could be made on the basis of their silica-sesquioxide ratios. R. S. Holmes (5) later showed that a specific soil type, Leonardtown, is characterized by constancy of composition. It was suggested by them, though they lacked definite proof, that the greater part of the silica, alumina, iron oxide, and water might be present as constituents of some mineral such as kaolinite, nontronite, halloysite, or pyrophyllite. Robinson and Holmes remarked: "With a further development of X-ray methods, it may be possible to decide definitely whether such complex mixtures as soil colloids are composed ultimately of crystals, and what compounds, if any, are present." The present work is essentially a consummation of this expressed hope.

MICROSCOPICAL EXAMINATION OF SOIL COLLOIDS

The colloids used in the following studies were extracted from soils by the method described in an earlier publication (4). The method limits the maximum size of the particles extracted to about 1μ; the greater part of the material is far smaller. Particles of this size are too small to admit of much observation in visible light and are far too small for the determination of the optical crystallographic properties in such light. These particles, however, have a tendency to orient themselves during the evaporation and drying of the suspension into the semblance of a regular cyrstallographic, or at least optical, arrangement as is shown from the petrographic examination. The mechanics of such a tendency, manifested even when the suspension was occasionally stirred, are not obvious. It might be suggested that if the colloidal particles are platy in

[1] The successful completion of this investigation was markedly aided by the assistance and advice of a number of people. Mr. R. S. Holmes, Mr. W. O. Robinson, and Dr. M. S. Anderson supplied the majority of the soil colloid samples examined. We are especially indebted to them and to Mr. Glen Edgington for analyses of the materials used. Dr. E. T. Wherry of the Bureau of Chemistry and Soils, and Dr. Clarence S. Ross of the Geological Survey of the Department of Interior kindly supplied us with fundamental information concerning the clay minerals. The success of the work, in a great measure, was due to the fact that pure samples of clay minerals were given to us by Dr. Ross. Mr. M. E. Jefferson did much of the X-ray photographic work.

shape (11) there would be a tendency for them to lie flat. The presence of predominantly platy minerals in the samples (see in the following), supports this hypothesis.

When the colloidal suspension was drying the particles agglomerated into masses large enough for petrographic study. The formation of aggregates and the orientation of the particles were perhaps subject to disturbing influences such as convection currents in the suspension, interference among the particles while settling, and cohesion. A specific soil colloid, as it will appear later, is not necessarily a single pure substance. For these reasons perfect optical reactions from the materials could not be expected, although such phenomena as interference figures and their modifications produced by the gypsum plate were surprisingly distinct.

Colloidal aggregates from a few soils were found to be opaque. Opacity itself is, of course, an optical property, but one that prevents the determination of other characteristics usually observed or measured in petrographic microscopic work. This property is always associated with a high iron or organic matter content. In mounts of even the most opaque of these colloids occasional doubly refracting aggregates were found. These, however, were deeply colored, translucent rather than transparent, and either failed to give interference figures at all or else gave figures of so vague an appearance as to be unrecognizable. Apparently the iron and organic matter is present in sufficient quantity to mask any doubly refracting material.

The double refraction of the large majority of the colloidal aggregates was surprisingly distinct. The interference colors ranged from the first to about the second order of Newton's scale and in some cases colors of an apparently higher order were noted.

The extinction was occasionally sharp, but in general it was wavy and sometimes absent, with the aggregate remaining bright during a complete rotation between crossed nicols. No spheroidal extinction was noted. The general wavy character of the extinction strongly suggested strain structure, but the study of the other optical properties of the aggregates made this belief untenable.

The interference figures were never perfect. Although the general shape of the hyperbolas and bars was easily recognizable and sometimes distinct, they were broad and blurred. The figures were, nevertheless, at least as good as and often better than those given by some minerals carrying a recognizable coating of colloidal material.

The blurred appearance of the interference figures made any measurement of the optic axial angle uncertain. In general this angle varied from zero up to about $2V = 30°$ or higher. Whether the figures that appeared to have a zero axial angle were actually uniaxial or were in reality biaxial with a small axial angle could not be decided with the imperfect figures obtainable. For this reason the listing of certain aggregates as giving unixial figures is purely tentative. The same sample of colloidal aggregates usually contained individual aggregates showing quite variable separations of the hyperbolas.

The optical character, determined with the gypsum plate, was perfectly definite except as noted in table 1. The refractive indexes of different aggregates in the same mount varied slightly. The values given are about the mean for the sample in question. It should be stated, however, that the colloidal aggregates were mostly more or less colored. For this reason perfect matching against the immersion oil was not possible. For these two reasons—variation of material and inaccuracy of determination—it is believed that a third decimal in the index figures would have been unjustified. Because of the imperfectly crystallized state of the aggregates and of their probable impurity, no effort was made to determine their indexes in different directions. The figures as given in table 1 represent simply the mean indexes.

The optical properties of the crystalline aggregates of the colloids examined are listed in table 1. Both decomposed organic matter and iron hydroxide are opaque in relatively thick sections. When present in sufficient quantity they effectively mask the presence of other substances. The observed scarcity of doubly refracting material in the Beckett, 0–6 inch, and the Superior, 3–8 inch, samples is probably due to the imperfectly crystallized state of the aggregates. The high iron content of the Nipe and Cecil samples accounts for the masking of the double refracting material in them.

Interference figures could not, of course, appear for samples free from doubly refracting material. Although there is but a small amount of doubly refracting material in the samples mentioned in the foregoing, some few particles could be observed. These particles were apparently quite impure. The results obtained from other samples (table 1) suggest that the Beckett, Superior, Cecil, and Nipe materials would also have given interference figures had there been less admixture with opaque substances.

The optical character of the aggregates, as determined on the interference figures by the gypsum plate, is predominantly negative. This is in accord with the known character of the clay minerals. Several samples, however, contained optically positive aggregates. The explanation for this is not known, but it might be suggested that quartz is positive. Quartz, as shown by the X-ray examination, is the only substance other than the clay minerals that is known to be present.

The refractive indexes given in table 1 are in general somewhat higher than those of the clay minerals shown to be present by the X-ray examination. The presence of free iron compounds in the aggregates is sufficient to explain this increase in index of refraction.

There is a partial correlation between the refractive indexes and the silica-sesquioxide ratio (table 2). In general, an increase in the silica-sesquioxide ratio is accompanied by a decrease in the refractive index. This change might be due to the concomitant variation in ferric oxide and alumina content. It can be said more truly that the refractive indexes fall into two large classes depending upon the silica-sesquioxide ratio. Numerous factors such as induration, chemical combination, and impurities probably combine to cause the observed irregularities.

X-RAY EXAMINATION OF SOIL COLLOIDS

X-ray technic

X-ray powder photographs were made from samples mounted in celluloid dissolved in amyl acetate, or from samples packed into very thin-walled glass

TABLE 1

A summary of the optical properties of soil colloids

COLLOID	DEPTH	DOUBLY REFRACTING MATERIAL	INTERFERENCE FIGURES	UNIAXIAL OPTICAL CHARACTER	BIAXIAL OPTICAL CHARACTER	REFRACTIVE INDEX
	inches					
Beckett	0–6	Scarce	None found	.....	.....	1.58
Beckett	6–11	Plentiful	Poor	.....	−(?)	1.57–1.58
Beckett	24–36	Plentiful	Poor	.....	−	1.60
Carrington	0–12	Moderate	Poor	.....	Indeterminate	1.57
Carrington	15–36	Plentiful	Poor	.....	−	1.57–1.58
Cecil	0–9	Scarce	None found	.....	.....	1.62
Cecil	9–18	Scarce	None found	.....	.....	1.62
Chester	0–8	Plentiful	Fair	−	.....	1.60
Chester	8–32	Plentiful	Poor	−	−	1.60
Clarksville	0–10	Plentiful	Fair	−	.....	1.59
Clarksville	10–36	Plentiful	Fair	.....	−	1.60
Fallon	0–12	Plentiful	Fair	−	.....	1.57
Huntington	0–8	Plentiful	Poor	−	.....	1.61
Huntington	8–30	Plentiful	Poor	−	.....	1.61
Manor	0–7	Plentiful	Poor	.....	−	1.59
Manor	7–20	Plentiful	Fair	−	+ and −	1.59
Marshall	0–14	Plentiful	Fair	−	−	1.58
Marshall	14–36	Plentiful	Fair	−	.....	1.58
Miami	0–10	Plentiful	Fair	−	−	1.59
Miami	10–24	Plentiful	Fair	−	−	1.59–1.60
Nipe	0–12	Scarce	None found	.....	.....	1.70
Norfolk	0–8	Plentiful	Fair	Indeterminate	+ and −	1.62
Norfolk	12–36	Plentiful	Fair	Indeterminate	+ and −	1.62
Ontario	12–22	Plentiful	Fair	.....	−	1.61
Orangeburg	0–10	Plentiful	Fair	+ and −	+ and −	1.60
Orangeburg	10–36	Plentiful	Poor	.....	+ and −	1.62
Sassafras	0–8	Plentiful	Fair	−	−	1.59
Sassafras	8–22	Plentiful	Fair	.....	−	1.59
Sharkey	0–4	Plentiful	Poor	.....	−	1.57
Stockton	0–38	Plentiful	Fair	−	−	1.57
Stockton	38–50	Plentiful	Fair	−	−	1.57–1.58
Superior	0–3	Scarce	None found	.....	.....	
Superior	3–8	Scarce	Poor	−(?)	−(?)	1.57–1.58
Superior	12–30	Plentiful	Poor	.....	.....	1.60–1.61
Superior	30–40	Plentiful	Poor	.....	.....	1.60–1.61
Wabash	15–36	Plentiful	Fair	−	.....	1.57–1.58

TABLE 2

Comparison of refractive index, silica, alumina, and iron oxide contents of soil colloids

SOURCE OF SAMPLE	DEPTH	SiO_2 RECALCULATED*	Al_2O_3 RECALCULATED*	Fe_2O_3 RECALCULATED*	$\frac{\text{MOLS } SiO_2}{\text{MOLS } Al_2O_3 + Fe_2O_3}$	REFRACTIVE INDEX
	inches					
Fallon	0–12	65.91	20.67	13.42	3.82	....
Sharkey	0–4	62.05	27.33	10.62	3.07	1.57
Stockton	0–38	59.94	27.26	12.80	2.87	....
Carrington	0–12	59.67	30.03	10.30	2.75	....
Superior	3–8	68.52	24.72	6.75	4.01	....
Wabash	15–36	62.42	25.77	11.82	3.33	....
Stockton	38–50	60.03	27.45	12.51	2.85	1.575
Beckett	6–11	68.52	24.72	6.75	2.85	....
Carrington	15–36	58.56	30.71	10.73	....	....
Marshall	14–36	60.07	27.43	12.50	2.87	....
Marshall	0–14	59.97	28.36	11.67	2.82	1.58
Beckett	0–6	.....	.....	.....	2.20	....
Miami	0–10	56.69	29.29	14.02	2.50	....
Clarksville	0–10	53.71	33.56	12.73	2.18	....
Sassafras	0–8	50.26	36.69	13.05	1.85	1.59
Manor	7–20	49.31	38.12	12.57	1.81	....
Manor	0–7	48.39	38.74	12.86	1.74	....
Miami	10–24	58.38	29.04	12.57	2.66	1.595
Clarksville	10–36	52.70	33.42	13.89	2.10	....
Orangeburg	0–10	49.51	38.09	12.40	1.83	....
Chester	8–32	48.85	37.32	13.84	1.79	1.60
Chester	0–8	48.60	37.36	14.04	1.77	....
Beckett	24–36	.....	.....	.....	1.67	....
Superior	30–40	55.14	28.77	16.09	1.79	....
Superior	12–30	45.01	35.81	19.18	1.59	1.605
Ontario	12–22	51.47	30.00	18.54	2.08	....
Sassafras	8–22	49.49	35.20	15.31	1.89	....
Huntington	8–30	49.65	33.61	16.74	1.89	1.61
Huntington	0–8	49.57	35.63	14.80	1.86	....
Norfolk	12–36	49.54	37.03	13.43	1.84	....
Orangeburg	10–36	48.21	39.25	12.04	1.71	....
Norfolk	0–8	47.39	38.67	13.94	1.67	1.62
Cecil	0–9	41.90	44.50	13.60	1.34	....
Cecil	9–18	39.72	47.75	12.52	1.20	....
Nipe	0–12	11.51	17.89	70.60	0.31	>1.70

* Recalculated on basis of $Fe_2O_3 + Al_2O_3 + SiO_2 = 100$ per cent.

tubes. Photographs were made with copper, iron, and molybdenum characteristic radiation. The casettes used with molybdenum radiation have radiuses of approximately 10 cm. and are hemicylindrical. Zirconium oxide filters were used for removing the MoK_β radiation. The X-ray tube used was operated at a peak voltage of 33 K. V. and a current of 15 M. A. A small cylindrical casette of 3.583 cm. radius was used with the copper and iron radiation. To produce these radiations the X-ray tube, an electron tube of laboratory construction, was operated under a tension of 20 to 30 K. V. and a current of 10 to 40 M. A. An oxide-coated platinum filament was used to prevent contamination of the anticathode, which, nevertheless, was cleaned at frequent intervals. A filter was not used with the copper and iron radiation.

Each pure substance examined has a characteristic powder diffraction pattern. It should be remarked that a mineral, of the type found, present as 10 per cent or less of the crystalline material of a sample would not be indicated by the diffraction pattern obtained. Truly amorphous material does not give an X-ray diffraction pattern. Mixtures of crystalline minerals with amorphous material give the diffraction pattern of the mineral. However, the contrast between the diffraction lines and the general photographic background is changed.

X-ray diffraction characteristics of pure clay minerals

A cursory examination of the X-ray powder diffraction patterns obtained from a few soil colloid samples indicated that the mineral present in each is closely related to kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). We were fortunate at this juncture in obtaining analyzed samples of carefully purified clay mineral.[2] The analyses together with the specific locality of the clay minerals used in this work are listed in table 3. Six distinct types of X-ray powder diffraction patterns were obtained from these minerals. The samples of montmorillonite and beidellite gave identical powder diffraction patterns. In the case of sample 4 (table 3), which is an iron-rich beidellite from Spokane, Washington, there is a definite change in the values of some of the interplaner spacings compared with those of the type of montmorillonite from Otay, California. Ross and Shannon (10) have assigned the formula $(Mg \cdot Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$ to montmorillonite. However, Wherry, Ross, and Kerr (12) have indicated that the ratio $SiO_2 : Al_2O_3$ might vary from 2/1 to 5/1, without change in structure; they commented that the compound

[2] From Dr. Clarence S. Ross of the U. S. Geological Survey, who with Prof. Paul F. Kerr of Columbia University is carrying out an extended investigation on the mineralogical, petrographic, and diffraction pattern characteristics of these minerals. Their work entirely supersedes the earlier descriptions given by Dana (3); it is, perforce, the basis for our investigation. We were kindly allowed to examine in manuscript a partial presentation of their results. The mineralogical and analytical material presented in this section is largely derived from that source; the X-ray diffraction results independently obtained are in accord with those of Professor Kerr.

probably does not have a definite silica to alumina ratio. Beidellite (10) has been shown to be essentially $Al_2O_3 \cdot 3SiO_2 \cdot nH_2O$. Here again wide variation in the silica-alumina ratio does not produce a noticeable change in physical properties including the X-ray diffraction patterns.

If these two suggested formulas, neglecting water, are written as $Ca_3Al_6Si_{12}O_{36}$ and $Al_8Si_{12}O_{36}$, it is seen that they differ chiefly in replacement of aluminum

TABLE 3

Analyses of pure clay minerals

	MONTMORILLONITE		BEIDELLITE		ORDOVICIAN BENTONITE	DICKITE	KAOLINITE		HALLOYSITE
	1	2	3	4	5	6	7	8	9
SiO_2	50.06	49.56	47.28	46.06	55.27	45.00	44.92	44.70	44.08
Al_2O_3	21.32	15.08	20.27	12.22	20.73	40.70	40.22	38.64	39.20
Fe_2O_3	0.22	3.44	8.68	18.54	2.18	tr.	0.54	0.96	0.10
FeO	tr.	.....	....	0.28	0.41	.....	.....	....	None
MgO	4.42	7.84	0.70	1.62	3.82	tr.	0.14	0.08	0.05
CaO	1.26	1.08	2.75	1.66	tr.	0.22	0.08	0.24	None
Na_2O	0.33	.....	0.97	.....	tr.	tr.	.....	0.62	0.20
K_2O	0.19	.....	tr.	.....	6.21	.....	.....	0.14	....
H_2O-	14.06	22.96	19.72	17.26	4.87	0.00	0.08	0.64	1.44
H_2O+	7.56				6.50	14.08	14.22	13.88	14.74
TiO_2	tr.	0.40	....	0.84	0.30	tr.	.....	0.22	tr.
SrO	....	.....	....	.....	N.F.	.....	.....	....	....
MnO	0.13	0.01	....	.....	N.D.	.....	.....	....	....
SiO_2/Al_2O_3	....	.....	....	.....	....	188/100	189/100	....	....

1. Pink, from a pegmatite, Pala, San Diego County, Calif., J. G. Fairchild, Analyst (Unpublished).

2. Bentonite, crude, selected pink material, near Otay, San Diego County, Calif., Earl V. Shannon, Analyst.

3. Beidellite gouge clay from Beidell, Sagauche County, Colo., E. S. Larsen and E. T. Wherry (6).

4. Iron rich beidellite; Spokane, Washington.

5. Ordivician bentonite, Evansville, Tenn.; J. G. Fairchild, U. S. Geol. Survey (unpublished).

6. Dickite, Gusihuiriachic, Mexico; J. G. Fairchild, Analyst (9).

7. Kaolinite, massive, from U. V. X. mine, Jerome, Ariz. Collected by F. L. Ransome; F. A. Gonyer, Analyst.

8. Kaolinite from one mile south of Ione, Amador County, Calif. F. A. Gonyer, Analyst.

9. Halloysite, Hickory, N. C., J. G. Fairchild, Analyst. (Unpublished).

by calcium, the ratio of silicon to oxygen remaining constant within the limit of error of analysis and the purity of the product. As is shown by sample 4, iron can partially replace aluminum with a resulting slight modification of the lattice.

The results of the investigations of Prof. W. L. Bragg and his co-workers on the structure of some silicate minerals show that quite often such compounds are structurally similar. Some structures are, for instance, based upon a

hexagonal or cubic close packing of oxygen atoms, with the smaller atoms of higher valence occupying interstitial positions (1). An examination of the X-ray diffraction data shows that the spacings and intensities of the lines cannot be explained on the basis of a simple close packing of oxygen atoms. The similarity of diffraction patterns, nevertheless, points to some common structural characteristics rather than to actual identity obscured by analysis of impure material. These minerals are far too complicated in structure to allow structure determinations without the use of very good crystals.

Crystalline kaolin minerals give diffraction patterns markedly different from those of montmorillonite-beidellite. The patterns of kaolinite, dickite, and nacrite can be easily differentiated from one another (see pl. 1, fig. 1 and table 4). The composition of these minerals can be represented by the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$; here again there is a wide variation in the observed silica-alumina ratio. Halloysite, from Hickory, N. C., gives a pattern closely similar to that of kaolinite, but different from it in relative intensities of reflection, in particular, of the planes of small spacings. The halloysite patterns were markedly poorer than those of dickite, kaolinite, or nacrite.

Potassium-bearing Ordovician bentonite, from Evansville, Tenn., shows a pattern similar to that of montmorrillonite, but differing from it by the presence of a number of extra lines. As shown in plate 1, figure 1, a mixture of montmorillonite and quartz gives a diffraction pattern very similar to that of the material from Evansville, Tenn. We hesitate at this time to describe the material as a separate type of mineral.

The six general types of photographs: montmorillonite, Ordovician bentonite, halloysite, kaolinite, dickite, and nacrite, together with that of quartz and a mixture of montmorillonite with quartz for comparison with ordovician bentonite are reproduced as figure 1. These photographs were made with copper radiation (K_α, = 1.53730 Å) unfiltered, in a cylindrical camera with a radius of 3.583 cm. The photograph of quartz is indicative of the quality of photographs obtained from materials composed of not too fine particles. Accurate determinations, from specific samples, of the spacings and intensities of reflection of the principal reflecting planes are listed in tables 5 to 7. Sodium chloride was used as a reference substance.

X-ray diffraction characteristics of soil colloids

Descriptions of the colloid samples, together with designations of the types of diffraction patterns given by them are listed in table 8. The analyses of the corresponding samples are given in table 9. Many of these are the same as were studied by Robinson and Holmes (7).

Some typical photographs representative of each type of pattern obtained from these colloid materials are shown in plate 1, figure 2. It is to be noted that in general the pattern is more diffuse and the background darkening, due to scattered radiation, is more pronounced than is the case for the pure clay

TABLE 4

A summary of x-ray powder diffraction data from Kaolinite and Dickite

KAOLINITE CLAY MINERAL				DICKITE CLAY MINERAL			
Angle	Line	Spacing	Intensity	Angle	Line	Spacing	Intensity
		Å				Å	
6° 11′	CuKα_1	7.15	s.	8° 53′	CuKβ	4.500	v.w.
10° 5′	α_1	4.39	m.w.	9° 51′	α_1	4.494	m.
10° 36′	α_1	4.18	v.w.	10° 38.5′	α_1	4.162	m.
11° 20′	α_1	3.912	v.w.	12° 25	β	3.232	v.w.
12° 22.5′	α_1	3.585	v.s.	11° 37.5′	α_1	3.815	m.w.
15° 42′	β	2.568	v.w.	12° 19′	α_1	3.605	s.
16° 10′	β	2.491	v.w.	12° 53.5′	α_1	3.446	v.w.
17° 26.5′	α_1	2.565	s.	13° 34.5′	α_1	3.276	v.w.
17° 58′	α_1	2.492	m.s.	14° 27′	α_1	3.08	v.w.
19° 9′	α_1	2.345	s.	15° 2′	α_1	2.96	v.w.
19° 37′	α_1	2.290	m.	15° 55′	α_1	2.802	w.
20° 31′	α_1	2.19	v.w.	17° 22′	α_1	2.574	m.s.
22° 47′	α_1	1.985	m.w.	17° 51′	α_1	2.509	m.
23° 31′	α_1	1.927	v.w.	19° 19′	α_1	2.329	v.s.
24° 40′	α_1	1.84	v.w.	20° 11′	α_1	2.221	w.
25° 37.5′	α_1	1.78	v.w.	20° 32′	β	2.19	v.w.
27° 38.5′	α_1	1.657	w.	22° 53.5′	α_1	1.976	m.s.
28° 21′	α_1	1.618	w.	24° 10′	α_1	1.88	v.w.
30° 3′	α_1	1.535	v.w.	24° 35′	β	1.67	v.w.
31° 10′	α_1	1.485	s.	26° 29′	α_1	1.725	v.w.
32° 7′	α_1	1.446	v.w.	27° 46′	α_1	1.651	s.
35° 18′	α_1	1.330	v.w.-w.	29° 0′	α_1	1.58	v.w.
36° 9′	α_1	1.303	m.w.	29° 30′	α_1	1.56	v.w.
37° 1′	α_1	1.277	m.w.	30° 6′	α_1	1.533	m.w.
38° 45′	α_1	1.228	v.w.	31° 6′	α_1	1.489	m.-m.s.
39° 34′	α_1	1.207	v.w.	31° 54′	β	1.316	m.w.
.....	..	.....	.....	32° 37′	α_1	1.426	m.w.-w.
.....	..	.....	.....	33° 31′	α_1	1.392	w.
.....	..	.....	.....	34° 7.5′	α_1	1.371	w.
.....	..	.....	.....	35° 46′	α_1	1.315	m.s.
.....	..	.....	.....	36° 53′	α_1	1.281	m.w.
.....	..	.....	.....	37° 51′	α_1	1.253	m.w.
.....	..	.....	.....	38° 33′	α_1	1.231	m.w.
.....	..	.....	.....	39° 5′	α_1	1.219	v.w.
.....	..	.....	.....	40° 22′	α_1	1.187	m.w.
.....	..	.....	.....	42° 13.5′	β	1.033	v.w.
.....	..	.....	.....	44° 12.5′	α_1	1.103	m.-m.w.
.....	..	.....	.....	45° 45′	α_1	1.073	m.w.
.....	..	.....	.....	47° 5′	β	0.948	v.w.
.....	..	.....	.....	48° 15′	α_1	1.031	m.
.....	..	.....	.....	48° 22′	α_1	1.028	v.w.
.....	..	.....	.....	51° 14′	α_1	0.985	m.w.
.....	..	.....	.....	52° 28′	α_1	0.970	w.
.....	..	.....	.....	53° 32′	α_1	0.956	w.-m.w.
.....	..	.....	.....	54° 10′	α_1	0.948	w.
.....	..	.....	.....	55° 8′	α_1	0.937	v.w.

TABLE 4—*Concluded*

KAOLINITE CLAY MINERAL				DICKITE CLAY MINERAL			
Angle	Line	Spacing	Intensity	Angle	Line	Spacing	Intensity
		Å				Å	
.....	..	.....	.....	55° 54′	α_1	0.928	m.w.
.....	..	.....	.....	57° 29′	α_1	0.912	v.w.
.....	..	.....	.....	59° 32′	α_1	0.892	v.w.
.....	..	.....	.....	60° 18′	α_1	0.885	m.
.....	..	.....	.....	61° 56′	α_1	0.872	w.
.....	..	.....	.....	63° 32′	α_1	0.859	m.w.

minerals (pl. 1, fig. 1). These facts are accounted for by smallness of particle size and by the possible presence of an amorphous constituent in the samples. Some of the photographs taken with copper radiation show a general photographic darkening due to the secondary iron radiation produced by the iron in the sample. Many of the samples were photographed with iron radiation without great improvement in the contrast except in those cases in which iron was present in large amounts.

The diffraction patterns obtained from soil colloids could be divided into three general classes; namely, montmorillonite, halloysite, and Ordovician bentonite. The close similarity of the pattern given by ordovician bentonite to that given by a mixture of montmorillonite and quartz (the optimum amount of quartz being 10 to 15 per cent) is particularly confusing in the case of the soil colloids. A differentiation between these two possible patterns could sometimes be made on the basis of variation in relative intensities of the lines obtained from the mixture due to changes in the amount of quartz present.

Accurate interplaner spacing and intensity measurements for three types of soil colloids—montmorillonite, Ordovician bentonite, and halloysite—are listed in tables 5 through 7. Data obtained from the pure clay minerals are listed for comparison. These measurements were made on photographs from samples of the soil colloid having a low amount of iron present. Sodium chloride was used as a reference substance. It is to be noted that within the limit of error the spacings are the same for the two groups of materials; especially when the poor character of the patterns obtained from the soil colloid samples is considered.

The diffraction patterns obtained from a few of the soil colloid samples were dissimilar to those of the previously described clay minerals. A very fine material separated from the C horizon of a Durham soil gave the same type of pattern as a sample of a corresponding Chester soil, namely, that of bauxite. It is to be noted that these samples have a very high alumina content. A Nipe colloid, characterized by a very high index of refraction, gave a distinctly different type of pattern but since it was not representative, no great effort was made to identify it. Neither these samples nor others examined showed the presence of limonite, hematite, magnetite, the common micas, or

TABLE 5

A summary of x-ray diffraction data from Montmorillonite type patterns

MONTMORILLONITE CLAY MINERAL				MONTMORILLONITE SOIL COLLOID			
Angle	Line	Spacing	Intensity	Angle	Line	Spacing	Intensity
		Å				Å	
8° 53′	CuKβ	4.499	m.w.	.....	..	.....	....
9° 51′	α_1	4.493	s.	9° 57′	α_1	4.44	s.
14° 32′	α_1	3.063	v.w.	.....	..	.....	....
15° 48′	β	2.550	v.w.	.....	..	.....	....
17° 32′	α_1	2.551	v.s.	17° 27′	α_1	2.56	s.
18° 4′	α_1	2.478	v.w.	.....	..	.....	....
24° 17′	α_1	1.869	v.w.	.....	..	.....	....
27° 9′	α_1	1.685	w.	26° 56′	α_1	1.697	w.
27° 47′	β	1.490	m.w.	27° 33′	β	1.501	m.w.
31° 3′	α_1	1.491	v.s.	30° 59′	α_1	1.493	v.s.
32° 32′	β	1.291	v.w.	.....	..	.....	....
36° 42′	α_1	1.286	m.w.	36° 32′	α_1	1.290	w.
38° 23′	α_1	1.238	m.w.	38° 12′	α_1	1.243	w.

TABLE 6

A summary of x-ray diffraction data from Ordovician bentonite (Montmorillonite-quartz ?) type patterns

ORDOVICIAN BENTONITE CLAY MINERAL				ORDOVICIAN BENTONITE SOIL COLLOID			
Angle	Line	Spacing	Intensity	Angle	Line	Spacing	Intensity
		Å				Å	
9° 56′	CuKα_1	4.45	s.	9° 53′	α_1	4.48	s.
12° 4′	β	3.321	w.-m.w.	11° 58′	β	3.35	m.w.
13° 23.5′	α_1	3.320	s.	13° 16′	α_1	3.35	s.
14° 28′	α_1	3.076	v.w.	.....	..	.....	....
15° 34.5′	β	2.587	w.-m.w.	.....	..	.....	....
17° 27′	α_1	2.565	s.	17° 27′	α_1	2.56	s.
18° 52′	α_1	2.376	v.w.	.....	..	.....	....
21° 4′	α_1	2.138	w.	.....	..	.....	....
22° 48′	α_1	1.984	w.	22° 42′	α_1	1.993	w.
25° 11′	α_1	1.807	v.w.	24° 53.5′	α_1	1.827	v.w.
26° 55′	α_1	1.698	m.w.	26° 53.5′	α_1	1.700	m.
27° 29′	β	1.505	w.	27° 41.5′	β	1.495	v.w.
28° 7′	α_1	1.631	w.	.....	..	.....	....
30° 51′	α_1	1.498	v.s.	31° 8′	α_1	1.487	v.s.
32° 19′	β	1.300	v.w.	.....	..	.....	....
34° 2′	α_1	1.372	m.	34° 2′	α_1	1.371	m.
36° 28′	α_1	1.293	m.s.	36° 23′	α_1	1.296	m.s.
38° 18′	α_1	1.230	w.	.....	..	.....	....
40° 2′	α_1	1.195	v.w.	39° 34′	α_1	1.207	v.w.
40° 39′	α_1	1.180	v.w.	40° 29′	α_1	1.184	v.w.

the common feldspars. Quartz was definitely shown to be present in several samples, notably the Sharkey colloids.

It is to be remarked that samples with high iron content often gave the halloysite type pattern. One might expect that replacement of aluminum by iron would produce a change in the interplaner distances. A slight change is produced by increased iron content in the case of the pure clay mineral beidellite, but there is no detectable change in the case of the soil colloids. Similarly the presence of excess magnesium oxide might lead to displacement of the diffraction lines; but close examination of the Fallon loam colloid showed no measurable effect. In both of the cases cited, change of spacing was tested

TABLE 7

A summary of x-ray diffraction data from Halloysite type patterns

HALLOYSITE PURE CLAY MINERAL				HALLOYSITE SOIL COLLOID			
Angle	Line	Spacing	Intensity	Angle	Line	Spacing	Intensity
		Å				Å	
10° 2.5′	α_1	4.41	....	10° 2.5′	CuKα_1	4.41	.....
.....	..	.....	....	12° 23′	α_1	3.584	.....
.....	..	.....	....	15° 37′	β	2.58	v.w.
16° 8′	β	2.50	v.w.	16° 8′	β	2.50	v.w.
17° 29′	α_1	2.560	s.	17° 26′	α_1	2.567	s.
17° 50.5′	α_1	2.508	m.s.	17° 49.5′	α_1	2.510	m.s.
19° 13′	α_1	2.337	m.s.	19° 16′	α_1	2.328	s.
.....	..	.....	....	19° 40′	α_1	2.284	m.
.....	..	.....	....	20° 38.5′	α_1	2.18	v.w.
.....	..	.....	....	22° 45′	α_1	1.988	m.w.
.....	α_1	1.680	m.w.	27° 20′	α_1	1.674	m.w.
28° 00′	α_1	1.637	m.w.	27° 58′	α_1	1.639	m.w.
.....	..	.....	....	30° 12′	α_1	1.528	m.w.-w.
31° 17′	α_1	1.480	v.s.	31° 17′	α_1	1.480	v.s.
.....	..	.....	....	32° 7′	α_1	1.45	w.
.....	..	.....	....	34° 19′	α_1	1.36	v.w.
37° 00′	α_1	1.278	m.w.	37° 5′	α_1	1.275	m.w.
38° 43′	α_1	1.229	m.	38° 39′	α_1	1.231	m.
.....	..	.....	....	40° 26′	α_1	1.185	.....

for by observing the line width in patterns obtained from mixtures of the specific material with standard samples of the type mineral.

Isomorphous replacement of one element by another must undoubtedly play a prominent rôle in the composition of these minerals. The X-ray photographs indicate that in such a replacement there is no great deformation of the lattice. The absence of pattern variation does not deny the possibility of variable composition.

It was desired to see whether or not colloid samples obtained from as widely different localities as possible and from varying depths in a specific locality but still belonging to the same soil type gave similar patterns. For this reason a study was made of a series of Leonardtown, Miami, Chester, and

Cecil colloids from localities as indicated and analysis as listed in table 10. With the exception of the Leonardtown colloids, the photographs from a particular series were the same in all but a few cases in which quartz was present as an impurity. The series of photographs obtained from the Cecil colloids with molybdenum radiation is reproduced in plate 2, figure 1. These photo-

TABLE 8

Type of x-ray diffraction pattern and refractive indices of soil colloids

SOURCE OF SAMPLE	DEPTH	TYPE PATTERN	RATIO SiO_2/R_2O_3	REFRACTIVE INDEX
	inches			
Sharkey Clay, Miss.	0–4	Montmorillonite-Beidellite (some quartz present)	3.07	1.57
Fallon loam, surface, Nev.	0–12	Montmorillonite-Beidellite	3.82	1.57
Houston black clay, surface, Texas	0–12	Montmorillonite-Beidellite	3.56	.....
Marshall silt loam, surface, Nebr.	0–14	Montmorillonite-Beidellite	2.82	1.58
Huntington loam subsoil, Md.	8–30	Montmorillonite-Beidellite	1.89	1.61
Sassafras silt loam soil, Md.	8–22	Montmorillonite-Beidellite	1.89	1.61
Iredell Clay subsoil, N. C.	6–24	Montmorillonite-Beidellite	1.93	.....
Beckett	6–11	Ordovician bentonite or Montmorillonite and quartz	2.85	1.575
Superior	3–8	Ordovician bentonite or Montmorillonite and quartz	4.01	1.575
Miami silty clay loam, surface, Ind.	0–10	Ordovician bentonite or Montmorillonite and quartz	2.50	1.59
Miami silty clay loam, subsoil, Ind.	10–24	Ordovician bentonite or Montmorillonite and quartz	2.66	1.595
Leonardtown, Md.	7–17	Ordovician bentonite or Montmorillonite and quartz	2.07	1.60
Leonardtown, hardpan, Md.	18–28	Halloysite	2.13	1.60
Cecil Clay loam, Ga.	0–9	Halloysite	1.34	1.62
Cecil Clay loam, Ga.	9–18	Halloysite	1.20	1.62
Cecil Clay loam, N. C.	5–36	Halloysite	1.18	1.62
Ontario loam, subsoil, N. Y.	12–22	Halloysite	2.08	1.61
Vega Baja clay loam, P. R.	0–12	Halloysite	1.34	.....
Chester loam, Md.	0–8	Halloysite	1.77	1.60
Chester loam, Md.	8–32	Halloysite	1.79	1.60
Chester	.....	Bauxite	0.68	1.60
Sub-colloid from Durham	.....	Bauxite with some clay mineral	....	.....
Nipe colloid	.....	Unidentified	0.31	>1.70

graphs are typical halloysite type patterns as produced with molybdenum radiation.

In the case of the Miami, Chester, and Cecil colloids, it will be noted that there are marked variations in gross analysis accompanied by a constancy of diffraction pattern. Colloids having a halloysite type pattern sometimes show

TABLE 9

Chemical analyses of soil colloids

NUMBER	SOIL TYPE FROM WHICH COLLOID WAS EXTRACTED	DEPTH	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	Cl	CO_2	IGNITION LOSS	COMBINED WATER	H_2O 110°	ORGANIC MATTER	N	MOLS SiO_2 / MOLS R_2O_3
		inches	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
4618	Amarillo, Texas†	0–5	50.51	0.56	22.04	8.80	0.14	1.48	2.08	2.68	0.06	0.20	0.18	.....	0.00	12.08	8.06	.....	4.02	0.33	3.10
4619	Amarillo, Texas†	10–20	51.51	0.57	22.71	8.61	0.09	1.59	2.66	2.54	0.01	0.12	0.14	.....	0.00	9.50	7.36	.....	2.14	0.25	3.09
4620	Amarillo, Texas†	30–40	51.32	0.58	22.43	8.46	0.05	2.27	2.80	2.50	0.06	0.14	0.14	.....	0.35	10.19	7.88	.....	1.96	0.13	3.13
4621	Amarillo, Texas†	54–64	51.23	0.55	24.68	8.19	0.07	1.73	2.83	2.42	0.10	0.11	0.13	.....	0.60	8.72	7.76	.....	0.96	0.08	2.97
4622	Amarillo, Texas†	70–75	38.42	0.37	17.64	5.71	0.06	16.38	2.53	1.83	0.06	0.09	0.10	.....	11.22	17.85	6.21	.....	0.42	0.07	3.21
4623	Amarillo, Texas†	96–100	45.88	0.52	20.09	6.89	0.05	9.05	2.87	2.26	0.01	0.11	0.13	.....	5.87	12.41	6.41	.....	0.13	0.05	3.18
4624	Beckett, Mass.†	0–6	10.58	0.49	5.99	3.64	0.02	0.65	0.31	0.49	0.25	0.31	0.99	.....	0.00	75.87	5.89	.....	69.98	....	2.16
4625	Beckett, Mass.†	6–11	38.39	1.48	20.26	5.55	0.02	0.40	1.03	2.51	0.24	0.25	0.23	.....	0.00	29.25	2.47	.....	26.78	....	2.74
4628	Beckett, Mass.†	24–36	34.31	0.72	27.55	11.60	0.01	0.17	2.10	4.10	0.25	0.18	0.19	.....	0.00	18.82	9.34	.....	9.48	....	1.67
....	Carrington, Iowa*	0–12	44.89	0.47	22.59	7.75	0.057	1.48	1.44	1.36	0.22	0.28	0.19	0.065	0.00	20.15	8.56	11.22	11.59	0.61	2.75
....	Carrington, Iowa*	15–36	48.04	0.65	25.19	8.80	0.032	1.29	1.53	0.89	0.38	0.14	0.08	0.037	0.00	13.75	9.23	10.98	4.52	0.20	2.64
....	Clarksville, Ky.*	0–10	42.40	0.81	26.49	10.05	0.372	0.62	1.22	1.76	0.25	0.65	0.21	0.045	0.00	15.60	9.89	10.21	5.71	0.38	2.18
....	Clarksville, Ky.*	10–36	43.68	0.63	27.70	11.51	0.150	0.48	1.39	1.65	0.34	0.38	0.09	0.031	0.00	12.79	10.51	8.00	2.28	0.20	2.10
....	Fallon, Nev.*	0–12	52.57	0.30	16.49	10.70	0.210	2.20	5.67	1.97	1.02	0.26	0.11	.....	.....	8.87	7.04	11.78	1.83	0.09	3.82
....	Hagerstown, Md.*	0–8	39.93	0.55	29.02	9.45	0.108	1.25	1.53	1.61	0.50	0.30	0.11	0.033	0.00	16.91	9.94	3.69	6.97	0.24	1.91
....	Hagerstown, Md.*	8–30	41.63	0.57	29.86	11.31	0.034	0.74	1.42	1.84	0.11	0.20	0.07	0.032	0.00	13.20	10.51	4.16	2.69	0.10	1.89
....	Huntington, Md.*	0–8	37.79	0.40	27.16	11.28	0.263	0.70	1.30	2.67	0.54	0.64	0.27	0.033	0.00	17.96	8.14	5.33	9.82	0.55	1.86
....	Huntington, Md.*	8–30	39.54	0.47	26.77	13.33	0.083	0.54	1.32	2.67	0.45	0.35	0.08	0.032	0.00	14.35	8.24	4.89	6.11	0.20	1.89
....	Manor, Md.*	0–7	38.86	0.72	31.11	10.33	0.112	0.64	1.23	1.37	0.63	0.28	0.09	0.029	0.00	15.63	11.94	4.63	3.69	0.21	1.74
....	Manor, Md.*	7–20	40.36	0.70	31.20	10.29	0.077	0.38	1.35	1.28	0.45	0.46	0.11	0.020	0.00	13.91	11.35	5.34	2.56	0.15	1.81
....	Marshall, Neb.*	0–14	45.93	0.48	21.72	8.94	0.066	1.19	2.01	2.28	0.21	0.46	0.21	0.060	0.00	16.47	7.92	7.75	8.55	0.51	2.82
....	Marshall, Neb.*	14–36	48.18	0.50	22.00	10.03	0.111	1.36	1.62	2.07	0.15	0.21	0.06	0.032	0.00	13.28	9.32	11.00	3.96	0.22	2.87
....	Nipe, Cuba†	0–12	10.19	....	15.84	62.51	.....	0.23	0.05	Trace	Trace	....	....	.....	.....	9.86	.....	.....	.....	....	0.31
....	Norfolk, N. C.*	0–8	38.25	0.79	31.21	11.25	0.033	0.54	0.53	0.26	0.09	0.23	0.08	0.047	0.00	16.51	11.92	4.45	4.69	0.22	1.67

....	Norfolk, N. C.*	12–36	41.60	0.71	31.10	11.28	0.005	0.34	0.49	0.46	0.22	0.26	0.05	0.028	0.00	13.81	11.50	3.25	1.60	0.25	1.84
....	Ontario, N. Y.*	12–22	42.40	0.56	24.71	15.27	0.138	1.18	2.59	2.39	0.51	0.25	0.06	0.028	0.00	10.71	7.22	9.50	3.49	0.23	2.08
....	Orangeburg, Miss.*	0–10	40.35	0.54	31.04	10.11	0.185	0.51	0.73	0.81	0.24	0.42	0.10	0.026	0.00	14.89	10.63	4.34	4.26	0.26	1.83
....	Orangeburg, Miss.*	10–36	40.35	0.44	33.27	10.08	0.595	0.45	0.67	0.81	0.29	0.17	0.09	0.024	0.00	13.60	11.92	5.44	1.68	0.25	1.71
....	Sassafras, Md.*	0–8	39.24	0.63	28.64	10.19	0.123	0.75	1.16	1.17	0.38	0.47	0.20	0.035	0.00	17.29	10.97	5.44	6.32	0.43	1.85
....	Sassafras, Md.*	8–22	41.14	0.70	29.26	12.73	0.031	0.53	1.07	1.35	0.42	0.08	0.07	0.020	0.00	14.08	12.49	5.32	1.59	0.32	1.89
....	Sharkey, Miss.*	0–4	51.34	0.51	22.61	8.79	.....	1.41	2.48	....	....	....	....	.....	....	10.93	7.45	9.30	3.48	0.57	3.07
....	Stockton, Calif.*	0–38	49.50	1.14	22.51	10.57	0.023	1.96	2.68	0.26	0.66	0.06	0.03	0.020	0.00	11.95	10.75	10.70	1.20	0.05	2.87
....	Stockton, Calif.*	38–50	48.61	0.94	22.23	10.13	0.063	1.70	3.37	0.78	0.50	0.20	0.04	0.019	0.00	12.51	9.69	8.76	2.82	0.07	2.85
4630	Superior, Wisc.†	3–8	46.20	0.97	16.67	4.55	0.08	1.01	1.25	2.14	0.34	0.39	0.35	.....	0.00	25.58	5.88	.....	19.70	....	4.01
4631	Superior, Wisc.†	12–30	31.60	0.88	25.14	13.47	0.08	0.66	1.71	1.37	0.15	0.96	0.18	.....	0.00	23.35	13.39	.....	9.96	....	1.59
4632	Superior, Wisc.†	30–40	42.20	1.57	22.02	12.31	0.12	0.61	3.41	1.23	0.06	0.31	0.17	.....	0.00	15.59	10.24	.....	5.35	....	2.40
....	Wabash, Neb.*	15–36	50.55	0.56	20.87	9.57	0.033	1.59	2.21	1.97	0.14	0.24	0.14	0.034	0.00	12.34	6.74	10.24	5.60	0.27	3.33

* Analyses taken from W. O. Robinson and R. S. Holmes (7).

† Analyses by Glen Edgington.

TABLE 10

Chemical analyses of colloids

NUMBER	COLLOIDS	DEPTH	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	
		inches							
....	Cecil,* Georgia	0–9	33.95	0.62	36.06	11.02	0.07	0.31	0
....	Cecil,* Georgia	9–18	31.84	0.53	38.28	10.04	0.06	0.35	0
3888	Cecil,† DeKalb County, Ga.	20–28	34.80	0.72	37.61	10.58	0.05	0.25	0
3889	Cecil,† Henry County, Ga.	18–30	32.42	0.76	39.93	10.70	0.08	0.29	0
3901	Cecil,† LaGrange, Ga.	10–42	36.77	0.72	32.55	13.67	0.05	Trace	0
3922	Cecil,† Rutherford County, N. C.	5–36	31.67	1.01	36.57	14.38	0.05	0.25	0
5101	Cecil,† Rutherford County, N. C.	0–5	33.02	0.97	35.24	10.77	0.09	0.21	0
5102	Cecil,† Rutherford County, N. C.	72–96	28.68	1.08	39.84	10.95	0.14	0.23	0
3462	Chester,† Cecil County, Md.	0–10	37.02	0.57	32.42	12.37	0.09	0.35	1
3464	Chester,† Cecil County, Md.	30–60	21.10	0.29	47.07	7.76	0.12	0.22	0
3454	Chester,† Cecil County, Md.	0–7	36.83	0.64	28.51	10.91	0.25	0.52	1
3455	Chester,† Cecil County, Md.	7–32	41.80	0.97	27.59	13.60	0.10	0.43	1
3456	Chester,† Cecil County, Md.	32–44	41.82	0.45	29.58	11.36	0.10	0.36	1
3457	Chester,† Cecil County, Md.	44–60	41.49	0.31	33.52	7.38	0.19	0.35	0
3911	Chester,† near Longwood, Pa.	3–8	28.17	1.14	28.18	16.10	0.00	0.61	3
3912	Chester,† near Longwood, Pa.	8–38	36.85	1.25	25.41	16.97	0.15	0.29	3
3913	Chester,† near Longwood, Pa.	38+	41.07	0.50	27.87	10.11	0.08	0.60	2
....	Chester,* Va.	0–8	39.00	0.58	29.98	11.27	0.03	0.93	0
....	Chester,* Md.	8–32	40.03	0.70	30.58	11.34	0.04	0.36	0
2250	Leonardtown,‡ Prince George County, Md.	7–17	40.70	0.80	26.44	12.88	0.04	0.38	1
2254	Leonardtown,‡ Prince George County, Md.	7–17	41.23	0.91	26.50	13.43	0.06	0.36	0
2512	Leonardtown,‡ Prince George County, Md.	12–18	42.99	0.80	27.30	12.17	0.03	0.21	0
2598	Leonardtown,‡ Charles County, Md.	7–14	42.54	0.85	26.85	13.03	0.02	0.36	0
2600	Leonardtown,‡ Charles County, Md.	7–14	41.07	0.76	26.82	13.09	0.05	0.23	0
2606	Leonardtown,‡ Prince George County, Md.	8–18	42.98	0.78	26.52	14.10	0.02	0.14	0
2608	Leonardtown,‡ Prince George County, Md.	8–18	41.87	0.84	27.41	13.78	0.07	0.39	0
3209	Leonardtown,‡ Prince George County, Md.	18–28	46.05	0.94	31.91	7.65	0.01	0.26	0
....	Miami,* Indiana	0–10	46.37	0.70	23.96	11.47	0.00	0.92	2
....	Miami,* Indiana	10–24	48.48	0.79	24.12	10.44	0.05	1.39	2
5092	Miami,† Grant County, Ind.	3–9	48.87	0.72	23.12	8.12	0.13	0.85	2
5093	Miami,† Grant County, Ind.	10–26	47.35	0.68	24.78	11.57	0.10	0.53	2
5094	Miami,† Grant County, Ind.	27–31	45.95	0.66	22.95	10.43	0.10	1.44	2
3967A	Miami,† Rush County, Ind.	30–34	45.79	0.53	24.37	12.71	0.13	1.33	2
3914	Miami,† Miami County, Ind.	6–10	47.00	0.57	22.85	9.40	0.23	0.91	1

* Analyses taken from W. O. Robinson and R. S. Holmes (7).

† Analyses by Glen Edgington.

‡ Analyses taken from R. S. Holmes (5).

TABLE 10
analyses of colloids

	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	Cl	CO_2	IGNITION LOSS	COMBINED H_2O	H_2O 110°	ORGANIC MATTER	N	$\frac{\text{MOLS } SiO_2}{\text{MOLS } Al_2O_3}$
2	0.17	0.31	0.40	0.56	0.44	0.25	0.06	0.036	0.00	16.67	14.42	3.23	2.25	0.22	1.34
4	0.16	0.35	0.23	0.46	0.28	0.11	0.02	0.023	0.00	18.00	16.56	4.93	1.44	0.11	1.20
8	0.0	0.25	0.78	0.30	Trace	0.06	0.18	.....	0.00	14.74	14.06	2.99	0.68	....	1.33
0	0.0	0.29	0.30	0.20	0.02	0.11	0.24	.....	0.00	14.90	14.10	2.57	0.80	....	1.18
7	0.0	Trace	0.05	0.19	0.13	0.02	0.27	.....	0.00	15.11	12.50	2.60	2.61	....	1.51
8	0.0	0.25	0.13	0.18	0.13	0.12	0.12	.....	0.00	14.13	13.01	2.00	1.11	....	1.18
7	0.0	0.21	0.54	0.34	0.06	0.25	0.20	.....	0.00	18.08	13.82	2.85	4.26	....	1.33
5	0.1	0.23	0.14	0.18	0.09	0.78	0.11	.....	0.00	17.37	16.51	3.27	0.86	....	1.03
7	0.0	0.35	1.19	0.94	Trace	0.38	0.18	.....	0.00	14.00	12.68	4.14	1.32	....	1.55
6	0.1	0.22	0.68	0.27	0.01	0.93	0.08	.....	0.00	23.74	21.08	....	2.66	....	0.68
1	0.1	0.52	1.39	1.00	0.13	0.45	0.34	.....	0.00	19.46	11.69	5.07	7.77	....	1.76
0	0.1	0.43	1.52	1.27	0.12	0.20	0.10	.....	0.00	12.22	10.42	4.48	1.80	....	1.98
6	0.1	0.36	1.34	0.92	0.10	0.22	0.15	.....	0.00	13.06	11.24	4.42	1.82	....	1.92
8	0.1	0.35	0.62	0.59	0.08	0.27	0.25	.....	0.00	15.02	12.12	3.39	2.90	....	1.84
0	0.0	0.61	3.86	1.30	0.09	0.84	0.43	.....	0.00	18.21	10.76	5.61	7.45	....	1.24
7	0.1	0.29	3.12	1.83	0.10	0.92	0.21	.....	0.00	12.47	9.58	4.82	2.89	....	1.69
1	0.0	0.60	2.19	1.44	0.56	0.74	0.28	.....	0.00	14.20	10.20	3.54	4.00	....	2.03
7	0.03	0.93	0.22	1.24	0.32	0.20	0.09	0.028	0.00	15.88	11.77	3.76	4.11	0.28	1.77
4	0.04	0.36	0.78	1.14	0.19	0.15	0.05	0.036	0.00	15.25	10.26	5.90	4.99	0.22	1.79
8	0.0	0.38	1.01	1.25	0.34	0.18	0.48	.....	....	15.74	10.94	....	4.80	....	1.99
3	0.0	0.36	0.85	1.25	0.29	0.19	0.32	.....	....	14.74	10.92	....	3.82	....	1.98
7	0.0	0.21	0.87	1.30	0.24	0.09	0.29	.....	....	13.67	11.40	....	2.37	....	2.07
3	0.0	0.36	0.67	1.03	0.36	0.15	0.18	.....	....	14.01	12.31	....	1.70	....	2.05
9	0.0	0.23	0.73	1.00	0.50	0.23	0.14	.....	....	15.58	12.60	....	2.98	....	1.98
0	0.0	0.14	0.90	1.40	0.26	0.18	0.19	.....	....	12.68	10.77	....	1.91	....	2.05
3	0.0	0.39	0.82	1.39	0.23	0.24	0.18	.....	....	12.89	10.58	....	2.31	....	1.97
5	0.0	0.26	0.49	0.67	0.20	0.17	....	.....	....	12.88	11.55	....	1.33	....	2.13
7	0.070	0.92	2.15	2.47	0.40	0.11	0.07	0.047	0.00	11.76	8.09	7.10	3.67	0.27	2.50
4	0.075	1.39	2.64	2.88	0.86	0.21	0.03	0.034	0.22	8.57	7.64	5.89	0.93	0.10	2.66
2	0.1	0.85	2.04	2.26	0.19	0.28	0.24	....	0.00	13.22	7.52	3.82	5.70	....	2.92
7	0.1	0.53	2.50	3.21	0 10	0.15	0.11	....	0.00	9.47	7.76	5.05	1.71	....	2.37
1	0.1	1.44	2.94	4.70	0.29	0.16	0.19	....	2.13	9.69	6.26	4.15	1.30	....	2.57
1	0.1	1.33	2.58	2.56	0.09	0.22	0.13	....	0.00	10.29	6.92	6.98	3.37	....	2.39
0	0.1	0.91	1.86	2.16	1.06	0.36	0.22	....	0.00	13.68	7.91	3.22	5.77	....	2.75

a silica-sesquioxide ratio as low as 1.0. This low ratio might be explained by the presence of a variable amount of an amorphous impurity, or by a variable composition of the clay mineral, halloysite, as previously indicated. This variable composition of the pure mineral might be due to the formation of solid solutions with other hydrous aluminum silicates.

A series of photographs of Leonardtown colloids shows that with but one exception the pattern is that of Ordovician bentonite or a mixture of montmorillonite with quartz. The hardpan from beneath a sample giving an Ordovician bentonite type pattern clearly gives a halloysite type pattern. Such a change is not entirely unexpected because of the obviously close structural similarity of the clay minerals. This one exception does not vitiate the general rule that a colloid of a specific soil type is characterized by the presence of an essential mineral constituent that does not vary from locality to locality (5).

A series of photographs, taken under identical conditions, of quartz mixed with amorphous aluminum silicate prepared by precipitation is shown in plate 2, figure 2. These patterns illustrate the increase in general scattering due to the presence of non-crystalline material. They are to be compared with those of the clay minerals, as is also the pattern of the homogeneous nickel oxide sample. In the case of the nickel oxide diffraction pattern it will be seen that the lines are very broad. This is due to the finely divided nature of the material, 10^{-5} to 10^{-6} cm. on the edge. Although the clay minerals and soil colloids gave markedly poor diffraction patterns, nevertheless it will be observed that the individual lines are rather well defined. The extra line width must sometimes be due to near superposition of two diffraction lines. There is no marked graduation of particle size over a large range, as would be suggested by a fuzziness of the lines. It is thus suggested that the crystalline clay minerals are not degenerated beyond a limit of about 10^{-5} to 10^{-6} cm. on an edge. The poor quality of the patterns is perhaps due to distortion of the small individual crystals.

DISCUSSION

It was impossible to answer the question whether or not the constituent giving the powder diffraction pattern was the only mineral present in the colloid. It should be remarked that with the exception of the presence of quartz in some samples the diffraction patterns showed the presence of only one crystalline component in each soil. This indicates that either the colloid sample is of uniform mineral composition or that only those minerals of the clay type retain their crystallinity sufficiently well to give an X-ray diffraction pattern. The primary soil minerals, such as micas, feldspars, and quartz, are not shown as crystalline components of the colloid fraction. Since these minerals can be microscopically identified in the parent soil, this rather indicates that they are not reduced, without chemical alteration, to small "colloidal" dimensions by natural processes, at least in the colloids examined.

Robinson and Holmes calculated the theoretical percentage of kaolinite and nontronite in a number of soil colloids. These calculations are based on the assumption that all of the silica is combined first with alumina to form kaolinite, then with the iron to form nontronite, given the formula $Fe_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ by Clark (2). With but one exception (table 9), that of Huntington loam, these colloids having excess silica, as indicated by Robinson and Holmes, have the montmorillonite type pattern. This indicates that the calculation based upon the assumed presence of kaolinite leads to the evident presence of free silica since in reality the mineral present, montmorillonite, has a higher silica-sesquioxide ratio.

Robinson and Holmes (7) point out that as the silica-sesquioxide ratio increases in the soil colloid there is a concomitant change in the lime soda-sesquioxide ratio ($CaO+Na_2O:R_2O_3$). In particular in the region near a silica-sesquioxide ratio of 2 to 1, the point of change from halloysite to montmorillonite, there is an increase in the lime soda-sesquioxide ratio. Ross and Shannon have concluded that montmorillonite contains $(Mg \cdot Ca)O$ as an essential constituent, the formula being $(Mg \cdot Ca)O \cdot Al_2O_3 \cdot 4\text{-}5SiO_2 \cdot nH_2O$. As previously pointed out there must be wide variations in the compositions of type montmorillonites. Here again there is indication that a constituent of the soil colloid, as shown by analysis, varies in a manner to be expected from the X-ray diffraction patterns.

Ordovician bentonite, as found in the United States, is a mineral of quite specific origin, namely, volcanic ash (8, 10). The analysis of Shannon shows that potassium is a prominent constituent of the type mineral. Considering these factors, its possible occurrence as a constituent of soil colloids seems rather surprising, especially since in the colloid samples there is no evidence of the presence of an unusually large amount of potassium. This, too, rather suggests that the material present in the soil colloids is a mixture of montmorillonite and quartz or else that potassium is not an essential constituent of the mineral.

In conclusion it can be said that the chemical correlations observed by Robinson and Holmes can be fully explained by the presence of montmorillonite, ordovician bentonite, and halloysite, as the characteristic minerals of the soil colloids.

Ross and Shannon (10) commented on the great variation in the amount of water present in samples of montmorillonite. From the fact that the water could be easily lost and regained and that during the process the physical properties of the minerals were not changed they suggested that the water is probably adsorbed. "This tendency to adsorb such large amounts of water is undoubtedly a function of the physical structure of the material which, *being extremely finely micaceous*, gives relatively enormous surface areas." The presence of the micaceous clay minerals as components of the soil colloids might explain some of the adsorption phenomena that characterize such materials. The absorption phenomena are perhaps also to be explained by the

presence of montmorillonite as a mineral that has a great amount of water of crystallization or constitution.

SUMMARY

Microscopical examination and X-ray powder diffraction photographs of the finely divided materials separated from soils by suspension methods show that these fractions contain crystalline substances.

A specific sample gives a characteristic powder diffraction pattern that can be identified as arising from one of the clay minerals.

By comparison with the powder diffraction patterns of known clay minerals, it has been shown that montmorillonite-beidellite, Ordovician bentonite (or a mixture of montmorillonite and quartz), and halloysite are the common mineral constituents of soil colloids. Bauxite was found to be present in two samples.

Fine fractions from a specific type of soil obtained from widely different localities give the same type of diffraction pattern.

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PLATE 1

TYPE CLAY MINERAL AND SOIL "COLLOID" DIFFRACTION PATTERNS

FIG. 1. Type Clay Mineral Diffraction Patterns. 1. Quartz; 2. Dickite; 3. Nacrite; 4. Kaolinite; 5. Halloysite; 6. Ordovician Bentonite; 7. Montmorillonite; 8. Montmorillonite-Quartz mixture; 9. Bauxite

FIG. 2. Diffraction Patterns of Soil "Colloids." 1. Bauxite; 2. Ordovician Bentonite (Montmorillonite Quartz); 3. Halloysite from Cecil Soil; 4. Halloysite; 5. Montmorillonite

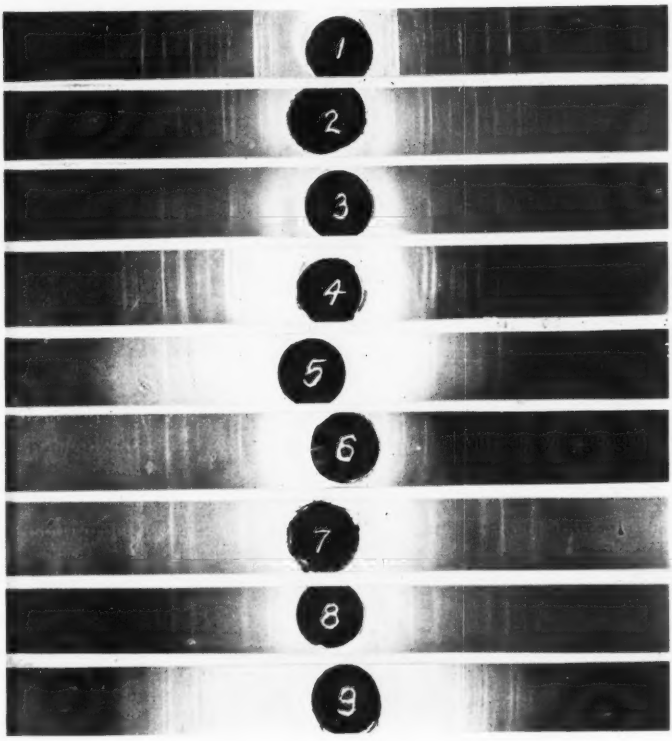

FIG. 1

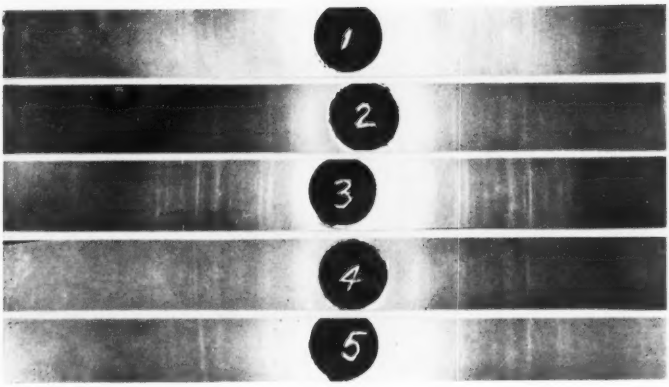

FIG. 2

PLATE 2

DIFFRACTION PATTERNS OF CECIL "COLLOIDS," AMORPHOUS ALUMINUM SILICATE, AND NICKEL OXIDE

FIG. 1. Series of Diffraction Patterns of Cecil "Colloids"; Mo K_α Radiation. 1. Cecil #5102 (see table 10); 2. #3922; 3. #3888; 4. #3889; 5. #3901.

FIG. 2. Quartz with Amorphous Aluminum Silicate and Nickel Oxide Showing Small Particle Size. 1. Nickel Oxide finely divided; 2. 25 per cent Quartz, 75 per cent Aluminum Silicate; 3. Quartz; 4. 50 per cent Quartz + 50 per cent Aluminum Silicate.

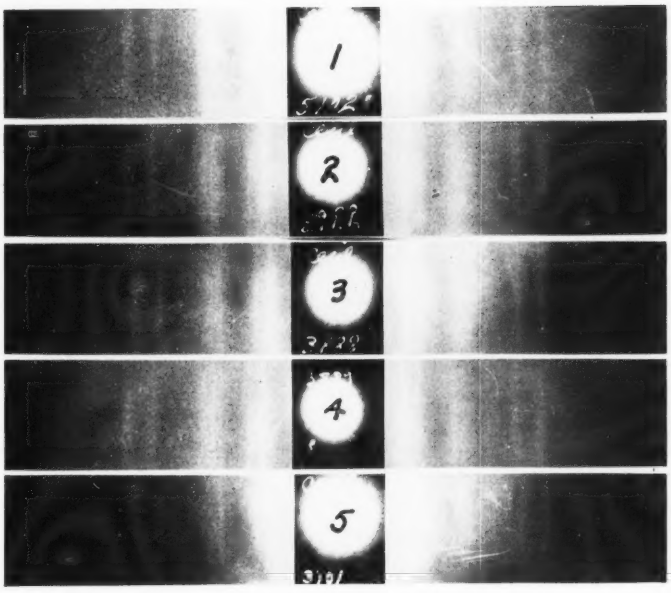

FIG. 1

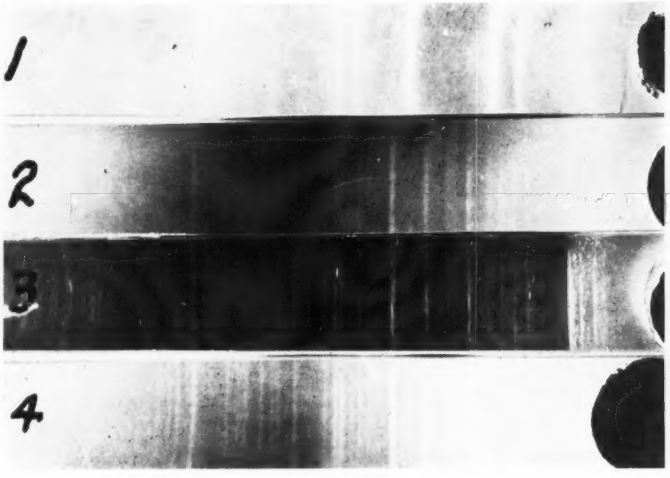

FIG. 2

PROPERTIES OF ORGANIC HARDPAN SOILS WITH SPECIAL REFERENCE TO THEIR FORMATION[1]

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Approximately one-half of the thirty-five million acres of land in Florida are classed as flatwoods soils. Since these soils are level and near an abundant supply of moisture, it would appear that they would be well adapted to the production of many cultivated crops. This is true only to a limited extent. Field observations indicate that whereas certain areas of the flatwoods are adapted to cultivated crops, other areas are not productive, although the surface characteristics of both soils are similar.

As a rule, those flatwoods soils having a low agricultural value contain a dark brown to black compact stratum 15 to 30 inches below the surface and 8 to 12 inches thick, commonly known as hardpan. Such soils are deceptive and disappointing to those attempting to farm them, except where the soil-water can be controlled through sub-irrigation systems. Unfortunately the water-controlled systems are limited to those localities in which flowing wells can be obtained. This means that Florida has a relatively large area of land with a low agricultural value.

The hardpan layer when well developed apparently hinders free movement of gravitational water during rainy seasons and capillary rise of moisture during dry seasons. Furthermore, the hardpan layer is usually too compact to permit root penetration of cultivated crops. This appears to be a mechanical rather than a toxic condition, as plants make a normal growth on the hardpan layer after it is broken up or removed from its natural position. It is generally accepted that organic matter is the cementing agent in the hardpan layer, although the cementing action of iron is evident in minor places.

The present study was undertaken to compare some of the basic properties of the hardpan soils with those of adjoining soils in the same locality, with the hope that such knowledge would lead to a better utilization of the hardpan soils.

[1] Contribution from the department of agronomy, University of Florida. Part of a thesis submitted to the graduate school of the University of Florida, in partial fulfillment of the requirements for the degree of master of science in agriculture.

[2] Research assistant, University of Florida Experiment Station. The author takes this opportunity to express his appreciation to Dr. O. C. Bryan for helpful suggestions and criticisms during the progress of this study.

EXPERIMENTAL

The soils used in this study were obtained from Hastings (St. Johns County) and Gainesville (Alachua County), Florida. These areas represented an irregular occurrence of the hardpan formation in small patches within the non-hardpan area under natural conditions, and offered an opportunity to compare the properties of the two types of soils adjoining. These soils are classified

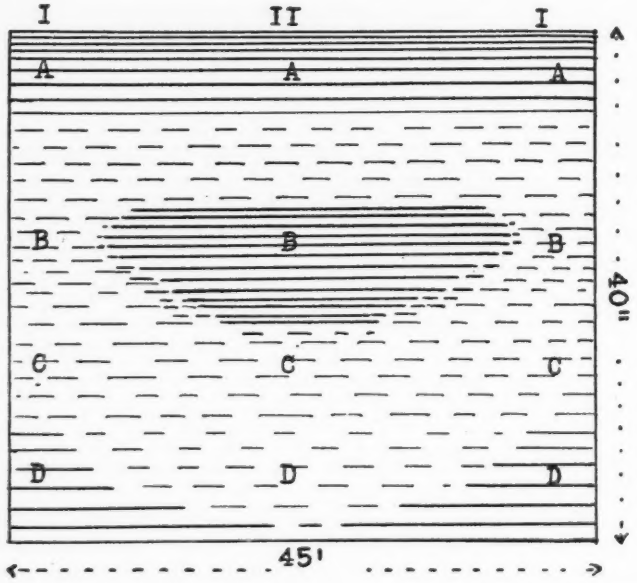

FIG. 1. A CROSS-SECTION OR PROFILE OF A HARDPAN AND NON-HARDPAN SOIL ADJOINING

I. Non-hardpan soil profile horizons:	
A. Sand	0–15 inches
B. Loamy sand	15–24 inches
C. Loamy sand	24–31 inches
D. Sandy clay	Greater than 31 inches
II. Hardpan soil profile horizons:	
A. Sand	0–15 inches
B. Compact layer	15–25 inches
C. Sand	26–36 inches
D. Sandy clay	36 inches or more

as Leon Fine Sand (hardpan) and Bladen Fine Sand (non-hardpan). Figure 1 shows the relation of the two soil profiles to each other. The different soil horizons are designated as A, B and C, respectively, as shown in the diagram. The hardpan in these areas was usually local and not quite so pronounced as the more typical hardpan soils in the state. Composite samples of horizons A, B and C, were taken with a soil auger from both the hardpan and the non-hardpan areas and were dried and stored for technical study.

The reaction of the different soils was determined colorimetrically with the LaMotte soil-testing set. The mechanical and chemical analyses were made according to standard methods. The carbon was determined by the modified combustion train method as outlined by Stetser and Norton (10).

REACTION STUDIES

It is generally thought that the reaction of the soil plays an important part in the formation of the hardpan in humid climates, but no data have been reported showing the comparative reactions of organic hardpan and non-hardpan soils within the same vicinity. For this reason the reactions according to the LaMotte test of the different soils were determined. The results are given in table 1.

Contrary to expectation, the H-ion concentration of the hardpan soils was slightly lower than that of the non-hardpan soils. The reaction of a great many other hardpan soils from different localities was determined but there was

TABLE 1

The hydrogen-ion concentration of hardpan and non-hardpan soils

HARDPAN SOILS				NON-HARDPAN SOILS			
Soil No.	Horizons			Soil No.	Horizons		
	A	B	C		A	B	C
	pH	*pH*	*pH*		*pH*	*pH*	*pH*
1	6.0	5.4	5.4	1	5.2	5.2	6.0
2	6.2	5.8	6.0	2	5.4	5.2	5.4
3	6.2	6.0	5.8	3	5.2	5.2	5.0

no significant difference between the pH value of horizon B (hardpan) and that of horizon A or C.

MECHANICAL ANALYSIS

If the formation of an organic hardpan is due to the downward movement of organic matter then the amount of silt and clay would be expected to affect this formation; that is, the finer the texture of the soil the less mechanical movement of organic matter downward. To test this assumption, the content of silt, clay, and fine sand in several adjoining hardpan and non-hardpan soils was determined according to the method outlined by Emerson (1). The results are given in table 2.

Although the content of silt and clay in the two soil profiles did not differ greatly, the surface of the non-hardpan soil had greater amounts than that of the hardpan soil. This difference produced a more plastic condition in the non-hardpan soil.

CHEMICAL STUDIES

Iron, aluminum, and calcium

If the formation of the hardpan was due to the solution, translocation, and precipitation of soil material, the content of iron and aluminum in the different

TABLE 2

Mechanical composition of hardpan and non-hardpan soils

SAMPLE NO.	HORIZON	FINE SAND		VERY FINE SAND		SILT AND CLAY	
		Non-hardpan	Hardpan	Non-hardpan	Hardpan	Non-hardpan	Hardpan
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	A	42.2	64.8	37.3	21.4	12.8	4.1
	B	49.8	47.5	33.9	31.0	8.3	9.0
	C	46.7	44.6	37.0	40.8	9.8	7.5
2	A	51.0	46.8	36.8	37.2	10.9	6.5
	B	50.8	46.7	31.2	39.2	6.0	4.6
	C	49.2	....	35.8	....	3.4	...
3	A	39.5	45.1	44.7	43.1	8.6	2.8
	B	....	40.7	....	43.8	....	6.0
	C	44.3	42.0	44.0	46.2	3.6	3.9

TABLE 3

Content of iron, aluminum, and calcium in the different horizons of non-hardpan and hardpan soils

SOIL NO.	HORIZON	Fe_2O_3		Al_2O_3		Ca	
		Non-hardpan	Hardpan	Non-hardpan	Hardpan	Non-hardpan	Hardpan
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	A	0.2412	0.1211	0.3002	0.0703	0.1122	0.0200
	B	0.1384	0.1251	0.0658	0.3829	0.0316	0.0394
	C	0.1542	0.1120	0.0494	0.0404	0.0269	0.0409
2	A	0.1357	0.1162	0.2951	0.0702	0.0876	0.0820
	B	0.1044	0.0908	0.2328	0.3074	0.0446	0.0345
	C	0.0747	0.0747	0.1569	0.1654	0.0306	0.0283
3	A	0.1025	0.0786	0.4398	0.0825	0.1423	0.0461
	B	0.1039	0.0871	0.3341	0.4653	0.0340	0.0261
	C	0.0746	0.1498	0.1293	0.2715	0.0230	0.0207

soil horizons should be very variable. To test this assumption, the content of iron, aluminum, and also calcium was determined in several hardpan and non-hardpan soils, according to standard methods. The results are given in table 3.

The data show no outstanding difference in total amounts of iron, aluminum,

and calcium in the two soil profiles. It may be noted, however, that the surface horizon of the non-hardpan soils contained a higher mean content of these elements than did the lower horizons; but this was not the case with the hardpan soils. In all instances the hardpan horizon contained a much higher content of aluminum than did either horizon above or below it. The accumulation of iron and calcium in the hardpan layer was negligible, but the decrease in iron from the surface downward was greater in the non-hardpan soil than in the hardpan soil. This would indicate a downward movement of iron in the hardpan soil. The most striking feature about the analysis is the high content of aluminum in the hardpan horizon.

Carbon-nitrogen determinations

If the organic matter in the hardpan layer has accumulated by the mechanical movement of the solid particles, then the relation between the carbon and nitrogen in the hardpan should closely resemble that of its parent material in the surface layer. On the other hand, the relation between the carbon and nitrogen in the corresponding layers of the non-hardpan soils would likely be different. For this reason the content of carbon and nitrogen in the different horizons of several hardpan soils adjoining several non-hardpan soils was determined. The results, together with the calculated carbon-nitrogen ratios for each horizon, are given in table 4.

From the data it may be seen that the surface of the non-hardpan soils contained more carbon than did the corresponding horizon of the hardpan soils. Furthermore, there is a decrease in nitrogen in all soils from the surface downward, but the rate of decrease is less in the hardpan profile. The results show that the carbon-nitrogen ratio decreases from about 15 to 6 with an increase in depth of the non-hardpan soils, whereas in the hardpan soils it was practically constant with an increase in depth.

DISCUSSION

If the hardpan was formed by the solution and re-precipitation of aluminum, it would appear that the factors causing this would also affect iron; but the results of this study show no concentration of iron in the hardpan layer, although there is a decided concentration of aluminum. Assuming that aluminum silicate (kaolinite, which is high in aluminum and almost free of iron), was present in the surface soil, it is possible that the translocation of this material is responsible for the concentration of the aluminum in the hardpan. It is also possible that an alkaline solution of the soil would bring aluminum into solution without dissolving the iron. It is doubtful, however, whether the soil was at any time sufficiently alkaline to cause this phenomenon.

The saucer-like depression in the clay layer under the hardpan (fig. 1) indicates an uneven clay surface before the overlying soil was deposited. These depressions were later filled with sand of a sufficiently loose nature to permit a downward movement of the colloidal organic matter with percolating

water. This assumption is supported by the fact that the hardpan layer is usually level and never overlaid with clay. No doubt the rainfall in Florida has depleted the soil of its soluble electrolytes, and hence dispersed the soil organic matter. This is substantiated by the dark-colored surface water (dispersed organic matter) in nearly all flatwoods soils in the state.

There is little proof that the dispersed colloidal organic matter is precipitated at the level of the water table. In fact the water table changes rather frequently as a result of irregular rainfall. However, it is possible that the pan formation had its initial beginning during a season of excessive rainfall. When once started, the infiltration process would be more plausible.

TABLE 4

Carbon, nitrogen and the carbon-nitrogen ratio in the different horizons of non-hardpan and hardpan soils

SAMPLE NO.	HORIZON	CARBON		NITROGEN		CARBON-NITROGEN RATIO	
		Non-hardpan	Hardpan	Non-hardpan	Hardpan	Non-hardpan	Hardpan
		per cent	*per cent*	*per cent*	*per cent*		
1	A	0.960	0.671	0.074	0.051	12.84	13.69
	B	0.335	0.818	0.035	0.049	9.29	16.69
	C	0.177	0.361	0.026	0.025	6.81	14.44
2	A	1.235	0.660	0.067	0.047	18.43	16.17
	B	0.480	0.516	0.041	0.037	11.71	13.95
	C	0.136	0.333	0.021	0.021	6.48	15.86
3	A	1.250	0.094	0.067	0.056	18.64	16.80
	B	0.180	1.630	0.022	0.086	8.00	18.90
	C	0.110	0.012	0.017	0.015	6.40	8.00 (Clay)
4	A	1.400	0.460	0.057	0.030	24.50	15.30
	B	0.270	0.690	0.021	0.037	12.86	18.70
	C	0.140	0.380	0.019	0.024	7.40	15.80

Many of the Florida sands having better drainage than the hardpan soils in question, contain a semi-hardpan several feet below the surface. Other sands have a brownish, irregularly colored subsoil. In places the subsoil is rather irregular, carrying small patches of hardpan. This would indicate that the soil texture affected the hardpan formation. In no instance was the hardpan layer in direct contact with clay and limestone, although these materials were noted underneath. Undoubtedly, clay and marl will filter the organic matter carried in percolating water.

It is possible that soluble electrolytes underneath brought about the initial stage of hardpan formation, particularly in lime rock areas. This would be local, however. The hardpan is usually found with sand above and below it.

The influence of the soil texture on hardpan formation is not definitely known. The results show no consistent difference in texture that may be con-

sidered worthy of note except in the content of silt and clay in the surface of the non-hardpan soil. This difference of 4 to 6 per cent could perhaps affect the movement of the organic matter. The uneven deposit of the hardpan layer would indicate a difference in texture in either the surface or subsoil.

The constant carbon-nitrogen ratio in the different horizons of the hardpan soil, compared to a gradual decrease from the surface downward in the non-hardpan soil, is explained on the assumption that the organic matter in the hardpan layer washed down from the surface soil and that the nature of the organic matter in all horizons is similar. On the other hand, the organic matter in the lower horizons of the non-hardpan soil was derived from the washing in of partially decomposed material from the surface soil.

It is doubtful whether the soils were ever more acid than at present (pH 5.6), especially in a humid climate. According to Morrison and Sothers (5), humic acid would not reduce ferric iron. This may explain why the iron did not accumulate in the hardpan layer. Furthermore, Skeen (9) reported that a reaction of pH 5.6 was not the most favorable for the solution of iron and aluminum. The concentration of the aluminum in the hardpan layer is more easily explained by assuming that kaolinite was brought down from the horizon above.

The results of this study support the work of Morrison and Sothers (5), Hissink (7) and others, in that the hardpan formation is due to the precipitation of dispersed soil organic matter and aluminum in certain soil horizons. This precipitation may be due to soluble electrolytes, soil texture, and a high water table.

Inasmuch as the hardpan and non-hardpan soils differ mainly in the presence of the hardpan layer, it seems quite possible that this layer could be mechanically broken, thereby rendering these soils more valuable for agricultural purposes, especially when the water table is lowered to prevent a recementing action. This phase of work is being studied further.

SUMMARY

A comparative study of hardpan and non-hardpan soils was made to ascertain the difference in reaction, texture, content of iron, calcium and aluminum, and carbon-nitrogen ratio. The results may be summarized as follows:

The reaction of the hardpan and non-hardpan soils was found to be almost identical.

The mechanical analysis showed less silt and clay in the hardpan than in the non-hardpan soils.

There was no definite concentration of calcium and iron in the hardpan horizon, but aluminum was very definitely concentrated.

The carbon-nitrogen ratio decreased from the surface downward in the non-hardpan soils, but remained almost constant in the hardpan soils.

The results indicate that under the climatic conditions of Florida, a loose sand, low in silt and clay and free of electrolytes, is favorable for the formation of an organic hardpan wherever the water table is near the surface (6 to 36 inches) during part of the year.

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AUTHOR INDEX

Alexander, J. Colloid chemistry; principles and applications (book review), 159.

Barnette, R. M., and Hester, J. B. Effect of burning upon the accumulation of organic matter in forest soils, 281–284.

Batham, H. N., and Nigam, L. S. Periodicity of the nitrate content of soils, 181–190.

Baver, L. D. Relation of the amount and nature of exchangeable cations to the structure of a colloidal clay, 291–309.

Blair, A. W. *See* **Prince, A. L.**

Buckman, O. *See* **Lyon, T. L.**

Büsgen, M., and Münch, F. The structure and life of forest trees (book review), 159.

Bushnell, T. M. The Purdue technique for taking and mounting monolithic soil profile samples, 395–399.

Christensen, O. An index of friability of soils, 119–135.

Clark, N. A., and Collins, E. R. Equilibrium between soil and electrolytes, and its influence upon some lime requirement methods, 417–427.

Clements, F. E. *See* **Weaver, J. E.**

Coles, H. G., and Morison, C. G. T. Dehydration and soil acidity, 59–70.

Collins, E. R. *See* **Clark, N. A.**

Conrad, J. P., Proebsting, E. L., and McKinnon, L. R. Equipment and procedure for obtaining the displaced soil solution, 323–329.

Degtjareff, W. Th. Determining soil organic matter by means of hydrogen peroxide and chromic acid, 239–245.

Doughty, J. L. The fixation of phosphate by a peat soil, 23–35.

Dreibelbis, F. R. *See* **Schollenberger, C. J.**

Emerson, P. Principles of soil technology (book review), 414–415.

Flint, Fred W. *See* **Smith, A.**

Fry, W. H. *See* **Hendricks, S. B.**

Ghosh, J. C., and Bhattacharyya, P. B. Removal of ions from solutions of calcium dihydrogen phosphate by treatment with hydrous gels of alumina, silica, and their mixtures, 311–322.

Greaves, J. D. The microflora of leached alkali soils: II. A leached sodium-chloride soil, 79–83.

Gericke, W. F. Plant-food requirement of rice, 207–225.

Hendricks, S. B., and Fry, W. H. The results of X-Ray and microscopical examinations of soil colloids, 457–479.

Hester, J. B. *See* **Barnette, R. M.**

Jenny, H. The nitrogen content of the soil as related to the precipitation-evaporation ratio, 193–206.

Kapp, L. C. The approximate size of soil particles at which the heat of wetting is manifested, 401–412.

Kappen, H. Die Bodenazidität (book review), 160–161.

Linford, L. B. Soil moisture phenomena in a saturated atmosphere, 227–237.

Löhnis, M. P. Can Bacterium radicicola assimilate nitrogen in the absence of the host plant, 37–57.

Losina-Losinsky, L., and Martinov, P. F. A method of studying the activity and rate of diffusion of protozoa and bacteria in the soil, 349–362.

Lutman, B. F., Microbiology (book review), 160.

Lyon, T. L., and Buckman, H. O. The nature and property of soils. A college text of edaphology (book review), 413.

MacIntire, W. H. *See* **Shaw, W. M.**

MacIntire, W. H., and Sanders, K. B. The fixation of the potash of a green manure by liming materials, 109–117.

McKaig, N., Jr. A holder for soil sample bags, 191–192.

McKinnon, L. R. *See* **Conrad, J. P.,** Proebsting, E. L., and.

Martin, T. L. The effect of alfalfa and sweet clover roots and tops on carbon dioxide evolution and accumulation of nitrates in the soil, 363–369.

Martinov, P. F. *See* **Losina-Losinsky, L.**

Metzger, W. H. Replaceable bases of irrigated soil, 251–260.

Morgan, M. F. Factors affecting the estimation of lime requirement from pH values, 163–180.

Morison, C. G. T. *See* **Coles, H. G.**

Münch, F. *See* **Büsgen, M.**

Nigam, L. S. *See* **Batham, H. N.**

Pierre, W. H. Neutralizing values and rates of reaction with acid soils of different grades and kinds of liming materials, 137–158.

Prince, A. L., and Blair, A. W. Soil and crop studies with ammonium sulfate, 267–279.

Proebsting, E. L. *See* **Conrad, J. P.,** and McKinnon, L. R.

Richardson, L. A. Properties of organic hardpan soils with special reference to their formation, 481–488.

Sanders, K. G. *See* **MacIntire, W. H.**

Schollenberger, C. J. Effect of leaking natural gas upon the soil, 261–266.

Schollenberger, C. J., and Dreibelbis, F.R. Effect of cropping with various fertilizer, manure, and lime treatments upon the exchangeable bases of plot soils, 371–394.

Sessions, A. C. Method for the determination of inorganic nitrogen in dried plant tissue, 285–289.

Shaw, W. M., and MacIntire, W. H. The nature of calcium hydroxide absorption by hydrated silica, 429–456.

Simon, R. H. The effect of phosphate and lime upon the rate curve of solubility of phosphorus from a Wooster silt loam soil, 71–78.

Smith, A., and Flint, F. W. Soil moisture determination by the alcohol method, 101–107.

Waksman, S. A. Impressions of certain soil conferences in Europe, during the summer of 1929, and some plans for the Second International Congress of Soil Science in 1930, 85–90.

Weaver, J. E., and Clements, F. E. Plant ecology (book review), 159–160.

Wheeting, L. C. A study of methods for the determination of the available potassium of soils, 1–21.

Wiley, R. C. Determination of calcium in the presence of iron and aluminum, 339–347.

Wilson, B. D. Exchangeable calcium and potassium in soils as affected by cropping and fertilization, 91–100; translocation of calcium in soils as measured by electrodialysis and plant growth, 331–337.

Wolfanger, L. A. The major soil divisions of the United States. A pedologic-geographic survey (book review), 415–416.

SUBJECT INDEX

Absorption—
  equilibria between silica and calcium hydroxide, 440.
  Freundlich, equation in silicon dioxide-calcium oxide absorption, 442.
  ion effect on, 443.
Alfalfa, effect on—
  carbon dioxide evolution in soil, 363.
  nitrate accumulation, 363.
Alkali soils, microflora of leached, 79–83.
Aluminum—
  "active" in soils treated with ammonium sulfate, 271.
  calcium determination in presence of, 339.
  gels—
    method of preparing, 312.
    removal of ions from calcium dihydrogen phosphate by, 311.
  precipitation of, in hardpan, 485.
Ammonia, exchangeable in soils, 383.
Bacteria—
  method of studying activity of soil, 349.
  radicicola—
    diffusion of, in the soil, 352.
    media for, 40, 47.
    nitrogen assimilation by, 37–57.
Base exchange, as affected by—
  cropping, 91, 371.
  fertilization, 91, 371.
  heating, 66.
  horizon, 256.
  lime, 371.
  manure, 371.
  soil moisture, 253.
Bases—*see* also Cations, Calcium-exchangeable.
  replaceable, of irrigated soil, 251–260.
Calcium—
  carbon dioxide effect on precipitation of, 344.
  determination of, in presence of iron and aluminum, 339–347.
  dihydrogen phosphate, removal of ions from with gels of aluminum, silicon dioxide, and their mixtures, 311–322.
  exchangeable—
    as affected by cropping and fertilization, 91.
    fertilizer treatment, 96, 99.
    method of determining in presence of carbonate, 94.
  exchangeable, relation to—
    cations, replaced by electrodialysis, 97.
    colloid content, 98.
    hydrogen-ion concentration, 95, 98.
    limestone applied in soil, 95.
    soil depth, 333.
  hydroxide, absorption of, by hydrated silica, 429–456.
  translocation of, in soils as measured by electrodialysis and plant growth, 331–337.
Capillary—*see* also Soil moisture.
  rise of water in tubes of soil, 230.
Carbon—
  dioxide—
    effect on calcium precipitation, 344.
    evolution of, as affected by alfalfa and clover, 363–369.
  nitrogen ratio—
    data, 204.
    in hardpan soils, 485.
Cations—*see* also Bases.
  exchangeable, relation to structure of colloidal clay, 291–309.
Clay—
  colloidal, structure of as related to exchangeable cations, 291–309.
  flocculation of colloidal, 296.
  hydrogen-ion concentration of, containing various cations, 293.
  migration velocity of colloidal, 294.
  minerals, X-ray diffraction characteristics, 462.
  particles, size of, formula for determining, 404.
  specific conductivity of colloidal, 294.
  viscosity of colloidal, 294.
Clover, effect on carbon dioxide evolution and nitrate accumulation in the soil, 363–369.

Colloid chemistry: principles and application (book review), 159.
Colloids—
chemical analyses of soil, 470.
clay, structure of as related to exchangeable cations, 291–309.
heat of wetting method for determining, 402, 408.
soil, X-ray and microscopic examination of, 457–479.
X-ray diffraction characteristics of soil, 464.
Electrode, quinhydrone, 421.
Electrodialysis, method of, 93.
Fertilizers—
ammonium sulfate effect on—
aluminum solubility, 271.
crop yields, 151, 268.
hydrogen-ion concentration of soils, 152, 270.
nitrogen content of crops, 272.
soil types, 267.
effect on—
exchangeable bases, 371.
exchangeable calcium, 96.
Forest trees, the structure and life (book review), 159.
Gas, natural, effect of leaking on soil, 261–266.
Gels—
alumina, removal of ions from calcium dihydrogen phosphate with, 311.
silica, removal of ions from calcium dihydrogen phosphate with, 311.
Hardpan—*see* Soils hardpan.
Heat—
effect on size of soil particles, 409.
of wetting in relation to size of soil particles, 401–412.
Humidity factor maps of the U. S., 195.
Hydrogen-ion concentration—*see* also Soils hydrogen-ion concentration.
cations in clay as they affect the, 293.
quinhydrone electrode for determining, in soils, 421.
Iron—
calcium determination in presence of, 339.
precipitation of, in hardpan, 485.
refracting materials in soil colloids as affected by, 458.
Lime—
effect on—
exchangeable bases, 371.
hydrogen-ion concentration of soil, 143, 147.
phosphorus solubility in soils, 71.
potash fixation, 109–116.
materials, relative value of different, 140.
neutralizing value of different grades of, 137–157.
reaction rate with different grades of, 137.
requirement—
hydrogen-ion concentration and, 163.
Jones method for, a modification, 165.
methods, influence of electrolytes on, 417–427.
titration method to determine, 425.
Magnesium, exchangeable, in soils, 381.
Manganese, exchangeable, in soils, 380.
Manure—
effect on exchangeable bases, 371.
green, fixation of potash from, by liming, 109.
Microbiology (book review), 160.
Microflora—*see* also Bacteria.
of leached alkali soils, 79–83.
Neubauer—
modification of the, test, 9.
potassium availability tests by the method of, 4, 7.
Nitrate—
accumulation of—
as affected by alfalfa and clover, 363.
during various seasons, 187.
content of soils, periodicity of the, 181–190.
Organic—
hardpan soils, properties of, 481–488.
matter—
as affected by burning of forests, 281–289.
method of determining, 239–245.
matter, relation to—
altitude, 194.
climate, 194.
Peat—
acidity of, as affected by heating, 63.
soil, fixation of, phosphate by a, 23–35.
Phosphate—
aluminum, solubility of, 29.
effect on solubility of phosphorus from a silt loam soil, 71.

fixation, as affected by—
aluminum chloride, 28.
calcium chloride, 26.
ferric chloride, 27.
hydrogen-ion concentration, 25.
iron, solubility of, 29.
Phosphorus solubility of soil, as affected by phosphate and lime, 71–78.
Plant—
ecology (book review), 159.
food requirement of rice, 207–225.
growth, translocation of calcium in soils as measured by, 331.
tissue, inorganic nitrogen in dried, 285.
Potassium—
available—
citric acid extract as a measure of, 16.
method of determining, 1–21.
Neubauer method of determining, 17.
steam as an agent of extracting, 17.
exchangeable—
in soils, 13, 381.
formula for determining, 14.
exchangeable, as affected by—
cropping, 91–100.
fertilizers, 381.
extraction of, with different solvents, 10.
fixation of, from green manures by liming, 109–117.
leaching, 109–117.
method of determining, 5.
Precipitation-evaporation ratio, relation to nitrogen of soil, 193.
Precipitation-temperature quotient map of U. S., 195.
Protozoa, method of studying activity of soil, 349–362.
Rainfall, *see* Precipitation.
Rice—
effect on replaceable bases, 257.
plant-food requirements of, 207–225.
Silica—
gels—
heat effect on absorption capacity of, 433.
method of preparing, 312, 430.
removal of ions from calcium dihydrogen phosphate by, 311.
hydrated, calcium hydroxide absorption by, 429–456.
Silicates, formation of, in the presence of silicon dioxide and calcium oxide, 449.
Sodium, exchangeable, in soils, 383.
Soil—
acidity—*see* also Lime.
as affected by gas leakages, 261–266.
as affected by heating, 63.
Bodenazidität (book review), 160.
buffer action and, 424.
dehydration and, 59–70.
bacteria, *see* Bacteria.
bases, replaceable of irrigated, 251.
colloids, *see* Colloids.
composition of, and compressive strength, 126.
conferences in 1929, impressions, 85–90.
constants for strength-moisture curves, 128.
divisions of the United States (book review), 414.
electrolytes, equilibrium between, and, 417–427.
extract as media for B. radicicola, 40, 51.
irrigated, replaceable bases of, 251–260.
lime, *see* Lime.
moisture—
capillary rise of, 230.
determination by the alcohol method, 101–107.
equivalent, relation to $CaCO_3$ absorption factors, 176.
methods of determining, a comparison, 101–106.
phenomena in a saturated atmosphere, 227–237.
relation to compressive strength, 126.
moisture, effect on—
diffusion of protozoa and bacteria, 353.
replaceable bases, 253.
nitrogen, relation to precipitation—evaporation ratio, 193–206.
organic matter, *see* Organic matter.
particles, size of, at which heat of wetting is manifested, 401–412.
peat, *see* Peat.
phosphate fixation by a peat, 23–35.
protozoa, *see* Protozoa.
profile—
monolith mounting, 395–399.
replaceable bases in, 256.
relation to ammonium sulfate, 267–279.
sample bags, a holder for, 191–192.
science, Second International Congress, 85–90.

solution—
equipment and procedure for obtaining the, 323–329.
specific resistance of, 327.
structure, effect on diffusion of bacteria and protozoa, 359.
Technology, principles of (book review), 414.
water soluble substances of the, as affected by heating, 67.
X-ray examination of, colloids, 457.
Soils—
acid, neutralizing values of different grades of lime on, 137–157.
alkali, *see* Alkali.
bases, exchangeable as affected by treatment, 371.
buffer effect of, 269.
calcium—*see* also Calcium, Lime.
exchangeable in, as affected by cropping and fertilization, 91–100.
translocation in, 331.
electrodialysis of, 93, 331.
forest, as affected by burning, 281–289.
friability of, 119–135.
hardpan, organic in, 481–488.
hydrogen-ion concentration—*see* also Hydrogen-ion concentration.
lime requirement and, 163–180.
quinhydrone electrode to determine the, 421.
hydrogen-ion concentration, as affected by—
ammonium sulfate, 152.
heat, 68.
liming materials, 143, 147.
Nature and properties (book review), 413.
nitrate content of, periodicity of, 181–190.
potassium—
exchangeable in, as affected by cropping and fertilization, 91–100.
methods for the determination of available, 1–21.
types of (textural), and potassium availability, 10.
Water-soluble soil constituents as affected by heating, 67.
X-ray examination of soil colloids, 457.

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